

AREA SELECTIVE GOLD THIN FILMS
BY METAL ORGANIC
CHEMICAL VAPOR DEPOSITION
ON TUNGSTEN THIN FILMS
PATTERNED ON SILICON

By

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Victor Evan House

To my wife, Inger,
and to my daughter, Aubrey.

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TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS.....	iii
ABSTRACT.....	vii
CHAPTERS	
I INTRODUCTION.....	1
Background.....	1
Gold Thin Film Deposition Methods.....	7
Chemical Vapor Deposition.....	11
II PHYSICAL AND CHEMICAL ASPECTS OF CVD AND SELECTIVITY.....	17
Pre-nucleation Processes.....	18
Physical Barriers to Nucleation.....	21
Chemical Barriers to Nucleation.....	24
III EXPERIMENTAL APPARATUS AND MATERIALS.....	26
Apparatus and Instrumentation.....	27
Candidate Gold Carrier Identification	
Test Ampule and System.....	27
Vacuum Sealed Ampule Construction.....	28
Compound Heating System.....	31
Laser System Description.....	31
Pulsed Radio Frequency MOCVD	
Reaction System.....	32
Pulsed radio frequency power	
generation system.....	32
Pulsed RF MOCVD reactor.....	34
Selectivity From Catalytic Activity	
Differences Apparatus.....	37
Apparatus for Optimum Deposition	
Parameters Identification.....	39
Thermal Desorption Mass Spectroscopy	
System.....	45
The vacuum console.....	45
The computer controlled mass	
spectrometer electronics system.....	51
Substrate and carrier compound	
heating system.....	52

Materials.....	53
Substrates.....	53
Gold Carrier Compounds.....	53
 IV EXPERIMENTAL METHODS AND OBSERVATIONS.....	 55
Gold Carrier Identification.....	55
Pulsed RF MOCVD Experiments.....	57
Selectivity From Catalytic Activity Differences.....	59
Wafer Precleaning Tests.....	65
Measurement of Carrier Vapor Pressure and Tungsten Reaction Probability.....	69
Identification of Optimum Deposition Parameters.....	69
Preliminary optimization tests.....	70
Systematic study of selective gold MOCVD.....	71
Analysis of gold films from the matrix study by SEM and EDS.....	74
Thermal Desorption Mass Spectroscopy.....	74
 V RESULTS AND DISCUSSIONS.....	 79
Gold Carrier Identification.....	79
RF MOCVD.....	80
Catalytic Differentiation of Surface Features for Selective MOCVD.....	83
Wafer Precleaning Study.....	84
Vapor Pressure and Tungsten Reaction Probability.....	85
Selective Film Deposition Parameters.....	89
Thermal Desorption Mass Spectroscopy.....	97
 VI CONCLUSIONS AND RECOMMENDATIONS.....	 120
 APPENDIX	
MASS SPECTROMETER CALIBRATION.....	122
REFERENCES.....	124
BIOGRAPHICAL SKETCH.....	130

Abstract of Dissertation Presented to the Graduate School
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Chairman: Samuel O. Colgate
Major Department: Chemistry

Area selective gold thin films were deposited on tungsten thin films that had been patterned on n-doped single crystal silicon wafers. Depositions were performed by metal organic chemical vapor deposition using triethyl phosphine gold chloride as the volatile gold carrier. The gold films showed excellent feature resolution and purity as demonstrated by scanning electron microscopy, energy dispersion spectroscopy, scanning Auger spectroscopy and sputter Auger spectroscopy. Typical gold films measured 4.8 microns thick and were grown in 1 hour.

Analytical results indicate that film growth on tungsten is catalytic while growth inhibition on silicon results from the critical size phenomena of stable nuclei formation. Thermal desorption mass spectroscopy experiments

performed during this study support this conclusion as reaction enthalpy changes for reductive elimination of chlorine are as much as 3 times higher on silicon than on tungsten.

CHAPTER I INTRODUCTION

Background

Electromigration and spiking problems associated with scaling of ubiquitous aluminum interconnects¹ in silicon based integrated circuit (IC) technology has spawned intensive research into solutions which either retain aluminum as the interconnect material or offer new interconnect schemes intended to replace aluminum altogether.² Both solution approaches require the incorporation of new materials in the circuit and new methods for their inclusion. The object of the present work is to describe research on a chemical method of thin film growth of gold on tungsten. Such a bilayer interconnect was first proposed early on in IC development when the above problems were first anticipated³, but until now no simple relatively inexpensive method for its formation has been described.⁴

The interconnect metallization provides on chip (IC) electrical communication routes between active devices such as the gates, sources, and drains of transistors. Scaling principles, as applied to conventional integrated circuits, were first described by Dennard.⁵ A reduction factor of α is assumed for all dimensions. For a material of constant

conductance, the interconnect line resistance and contact resistance (interconnect contact to active device feature) increase by α and α^2 , respectively. Since the standard operational voltages (TTL logic levels) have remained essentially the same, scaling produces spiking of aluminum into underlying silicon structures resulting from solid solubilities of the interconnect metallization with semiconductor material due to the increased Joule heating effects at contacts where power dissipation also scales as α^2 . However, the most severe ramifications of interconnect scaling are the open line and shorting failures caused by voids and hillocks resulting from the electromigration of conductor atoms as current densities scale by a factor of α .⁶

Electromigration results from the opposing electrostatic and collisional forces (commonly called the "electron wind") operating between flowing electrons and charged conductor centers. Electromigration problems are rarely encountered in bulk materials since, for a standard #14 gauge household wire, currents of 4000 to 40,000 A would be necessary for its manifestation. Current densities in the range of 2×10^5 to 2×10^6 Acm⁻² are typically encountered in integrated circuits and the resulting Joule heating effects are tolerable only because of the intimate contact of the interconnect with the high thermal conductivity and relatively high thermal capacity of the underlying silicon.⁷ In an interconnect element,

electromigration can be observed only where a region of conductor flux divergence occurs. The conductor flux is a function of its temperature (T), current density (j), and average crystal grain size (q) for which the mass transport flux vector $\vec{J}$ has the form

$$\vec{J} = f(T, j, q) \quad \text{I.1}$$

The divergence of this flux vector is defined by

$$\nabla \cdot \vec{J} = \frac{\partial \vec{J}}{\partial T} + \frac{\partial \vec{J}}{\partial j} + \frac{\partial \vec{J}}{\partial q} \quad \text{I.2}$$

The divergence has the following physical meaning when considering electromigration failures in thin films. In any region having a zero divergence, as much mass flows in as flows out. In any region of the film having a positive divergence, more mass flows out than in and, therefore, voids form. Finally, in any region having a negative divergence, more mass flows in than flows out and, hence, hillocks form. Expressions for electromigration fluxes based on mobile atom statistical distributions have been developed by Hunigton and Grone⁸ and by Ho and d'Heurle.⁹ Their work shows that the primary contribution to electromigration in real circuits results from inhomogeneities in the microstructures of the films. Specifically, it has been shown that serious electromigration problems appear in pure aluminum films at

current densities greater than 10^5 A/cm² while gold films do not experience serious problems until current densities exceed 10^9 A/cm².³ With regard to the above mentioned current densities encountered in present circuits, gold usage would appear to offer distinct advantages.

Efforts to reduce electromigration in current aluminum usage involve primarily the inclusion of small amounts of copper in the aluminum lines during deposition. While the concomitant resistance to electromigration is improved by up to 3 orders of magnitude (based on mean time to line failure), hillock formation will still occur during manufacturing heat treatments unless the copper concentration is adequately high.¹ The higher copper concentrations make process etching more difficult due to the corrosive behavior of copper. Also, copper can diffuse slowly into surrounding oxide layers degrading underlying devices.¹⁰ For high speed circuit operation, though, the most severe penalty is the nearly 10-30% increase in resistivity over pure aluminum.¹¹ The characteristic response time associated with a fine line interconnect on an insulating film is measured in terms of its RC constant as

$$RC = \frac{\epsilon R_s l^2}{t} \quad \text{I.3}$$

where R_s and l are the sheet resistance and length of the interconnect line and ϵ and t are the dielectric constant

and thickness of the insulating film, respectively.^{12,13} Since the RC constant remains unchanged by scaling, circuit operational speed improvements resulting from the scaled down devices can be reduced when additives that increase sheet resistance are used.

Solutions to the spiking problem also include incorporation of resistance increasing additives in aluminum, in this case the usual additive is silicon. The spiking problem results from the high solubility of silicon in aluminum. During high temperature processing or at contacts operating at increased temperatures from high current densities, the underlying semiconductor material serves as a reservoir for silicon which rapidly diffuses into the aluminum. Simultaneously, voids formed in silicon are occupied by aluminum. If the penetration of aluminum is deeper than the p-n junction depth below the contact, the junction will be electrically shorted.¹¹ Thus, by satisfying the aluminum/silicon solubility during processing spicing is prevented, but propagation delays are increased. The added silicon concentration requirements are quite narrow and difficult to fulfill during processing. Difficulties with silicon precipitation during post addition anneals, etching and operation have also been encountered.¹⁴ Other solutions include the use of high resistant silicide barriers such as $PtSi$ or $PdSi_2$, which themselves pose increased processing complexity.¹⁵ In consideration of the problems associated with aluminum

metallization, and the drawbacks to potential solutions for its usage retention, it is clear that for continued down scaling of high speed integrated circuits new metalizations must be used.

Among the elements, only aluminum, copper, silver and gold have low enough resistivities to be used as interconnects in high speed devices operating at room temperatures.¹⁶ Problems with copper solubility and corrosion have already been described and silver exhibits these problems at even more severe levels. To be sure, much recent work on the use of copper as a replacement metal for aluminum has been performed.^{17,18,19,20,21,22} Due to the silicon/silicon oxide solubility problems, though, the copper lines must be encapsulated in order to ensure circuit stability. Also, problems with grain coalescence in deposited films result in elevated resistivities. Gold, on the other hand, is relatively inert in process ambients. Its low resistivity is compatible with small propagation delays. Its superior and well studied resistance to electromigration were noted above. Its high solubility in silicon and silicon oxide, however, precludes its usage as a direct contact to silicon and necessitates the use of a barrier conductor.

Numerous barrier materials are now in development and include TiN, various metal silicides, and several refractory materials and their alloys.^{23,24} Of the potential barriers, tungsten appears to offer many advantages. Tung-

sten has a relatively low resistivity ($5.5 \mu\Omega\text{-cm}$) and can form low resistant contacts to silicon. The most notable attribute of tungsten for this use is its ability to be deposited selectively at submicron dimensions by metal organic chemical vapor deposition (MOCVD) on silicon to the exclusion of deposition on silicon oxide.^{25,26} To be sure, tungsten alone is now in limited use as a replacement metalization for aluminum,^{27,28} but its resistivity, more than double to that of aluminum and gold, is not compatible with high speed devices.

Gold Thin Film Deposition Methods

There are six general methods available for producing gold thin films for use in integrated circuits:

- 1) electroplating
- 2) sputtering
- 3) vacuum evaporation
- 4) ionized cluster deposiiton
- 5) molecular beam epitaxy
- 6) chemical vapor deposition

The first five are described in this section. Chemical vapor deposiiton is described in a separate following section.

Electroplating gold from solutions has been used extensively in electronics to form thin film structures with dimension greater than several microns.²⁹ Typically these films are quite porous and have significantly lower

conductivities than bulk gold. Alkali ions which commonly occur as impurities in gold electroplate also present contamination problems as they tend to migrate in electric fields and accumulate at junctions thus changing device operational characteristics. Problems with dendritic growth in electroplated gold films lead to short circuits in adjacent conductors.³⁰ Improvements in conventional electroplating have been developed using a laser enhanced jet plating technique.³¹ The method produces high quality gold spots and lines by rastering an argon-ion laser beam passing through a jet of electrolyte and focussed on the cathode surface. While deposition rates of 30 microns/sec. were reported, the inherently low throughput of raster techniques precludes their use in mass production.

Sputtering is a physical vapor deposition technique in which ionized gases (usually argon) bombard a target composed of the metal to be deposited. The energetic ion collisions dislodge surface metal atoms which then travel to the substrate where they are deposited. Patterns are formed through masks during deposition or by post deposition etches. Variations have been developed which include the addition of reactive gases to the deposition chamber or heating and/or application of a radio-frequency potential to the substrate. These modifications can improve step coverage over circuit features, which is essential for small scale device and interconnect formation.^{14,32,33,34} These improvements have not, however, completely solved the step

coverage problem for small dimensions, and the method is still considered non-conformal.³² Conformal coverage refers to the ability of a film to be evenly deposited on all surfaces of a substrate, regardless of the geometric diversity. Because of the intrinsic high cost of gold, its use in sputtering would necessitate inclusion of expensive recovery steps to reclaim gold deposited on masking materials or material removed from substrates by etching.

Vacuum evaporation is also a physical vapor deposition technique that employs heating by convection, resistance, laser, or electron gun to volatilize the metal in a vacuum. The evaporated material then travels by line of sight to the substrate where it condenses forming a thin film.³¹ Masking or etching are used to form patterns. The method is also non-conformal and shares the material recovery problem associated with gold sputtering.

Ionized cluster beam deposition utilizes ionized metal clusters of up to several thousand atoms to form thin films.³⁵ The clusters are formed by homogeneous or heterogeneous nucleation either in the vapor phase from the plume exhaust of a nozzle fitted into a hot crucible containing the molten source material, or on the side walls of the crucible itself before exiting through the nozzle. The clusters are subsequently ionized by electron bombardment then accelerated to high voltage and directed at the substrate surface. The accelerating potential is controlled such that substrate incident clusters arrive with

energies below that which would induce surface damage, yet high enough to acquire fluidity and thus substantial surface mobility. High quality thin films can be formed this way at low substrate temperatures. Patterning is achieved by a post deposition etch. Studies have shown that only 1% of the total metal flux from a crucible filled with molten gold or silver was in the form of clusters in a usable size range.³⁶ This technique does not presently appear useful for gold thin film mass production.

Molecular beam epitaxy is a deposition technique typically performed at ultra-high vacuum ($<10^{-9}$ torr). Films grown under these conditions can be atomically abrupt with well controlled interfaces.³⁷ The method typically employs electron beam evaporation of the material to be deposited. Vapors travel by line of sight to the substrate surface which has previously been subjected to thorough in situ cleaning by sputtering and high temperature bake-out. Typically, a molecular beam epitaxy system contains sophisticated surface analytical devices for the direct measurement of surface contamination. The cleaning steps are the key to growing films epitaxially, as defects and contaminations in the surface act as nucleation centers for lattice defects. Low through-put and the high expense of the elaborate equipment preclude its usage as a deposition technique for gold interconnects, but the method is very useful for forming specialized and novel circuit devices.³⁸

Chemical Vapor Deposition

Chemical vapor deposition (CVD) is apparently the only available metallization technology type that can meet the requirements of high through-put for mass production as well as offer selectivity for the elimination of masking. Selective CVD offers the further advantage of elimination of waste material recovery steps since source material could be recycled in situ. This feature is especially attractive with the use of gold. Films are typically of high quality, purity and conformal step coverage. Because CVD is the deposition methodology of the present work, an in depth treatment of its salient features is given below.

Chemical vapor deposition can be described as the formation of a non volatile film by the decomposition or reaction of a volatile carrier molecule at a surface. In an ideal CVD process decomposition or surface reaction results in the desired film constituents remaining on the surface while all other products are themselves volatile and thus desorb from the deposition supporting surface. Selective CVD is an identical process with the constraint that the reaction is confined only to desired surface regions either by taking advantage of intrinsic surface chemical or physical attributes such as catalytic or low surface tension areas,¹³ or by imposing differences as in the heating of localized areas as in laser direct writing.

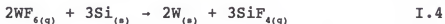
The cornerstone for modern CVD technology was set in place in 1852 when Bunsen reported the vapor transport of

iron from volcanic gases.³⁹ Saint-Claire Deville extended this work when he reported "the artificial reproduction of crystalline minerals" from the formation and subsequent decomposition of volatile chlorides of tin, titanium and magnesium formed by passing HCl over their respective oxides.⁴⁰ The first reported application of a CVD technique was in 1893 by de Lodyguine, who attempted to coat the carbon filaments of incandescent lamps with tungsten in a mixture of H₂ and volatile WCl₆.⁴¹ Before the proliferation of CVD usage in the electronics industry in the 1950s, vapor deposition techniques were primarily used for the purification of certain metals such as nickel.^{42,43} The first work on gold vapor deposition was performed by Blitz, Fischer, and Juza, who studied the gold/chlorine equilibrium.⁴⁴ Deposition of gold thin films from numerous metal organic compounds was first reported by Mann, Wells and Purdie in 1937.⁴⁵ Surprisingly, though, interest in gold CVD for commercial application has appeared only recently.^{4,46,47,48,49}

Although a few area selective CVD chemistries were known as early as 1971 for the deposition of germanium and gallium arsenide,^{50,51} only recently has it become a topic of wide spread interest. This interest has been spawned by the miniaturization trends in microelectronics as lithographic methods of circuit patterning have become stressed by the smaller feature dimensions.⁵² The primary focus has been on selective deposition of metals for

interconnects such as aluminum⁵³, copper^{17,20,21}, tungsten(also as a barrier)^{51,54,55,56}, and the present work with gold⁴.

There are three basic reaction types involved in these processes. The sacrificial method depends on a reaction of the carrier molecule with the base substrate material and thus consumes some of the substrate. For example one selective tungsten method on silicon employs WF_6 in the reaction⁵⁷



In this process an oxide layer is first formed on the silicon surface then patterns are etched through it exposing underlying silicon. The surface is then exposed to the tungsten bearing vapor. The reaction is confined only to areas of exposed silicon. Since the reaction is dependent on the diffusion of WF_6 to the substrate material, it is self limiting at about 1 micron thickness.

The second type of reaction involves the selective adsorption of a gas which reacts with the metal bearing vapor. This method is also used for the reduction of WF_6 on silicon by the reaction⁵⁷



Again, the silicon surface is first oxidized and patterns etched in the surface. Hydrogen adsorbs preferentially on the exposed silicon and on the growing tungsten film thereby confining the reaction to the desired areas. This method is used in combination with the method of reaction I.4 to grow thicker films. The advantage of the sacrificial reaction is

that it yields lower resistant, more adherent contacts to silicon. The third type of selective reaction, and the type for the focus of the present work, employs either damaged or pre-nucleated surfaces (pre-nucleated with either the material to be deposited or another material) to promote reaction on desired regions. Thus for aluminum, an aluminum line was pre-nucleated on quartz using an Ar^+ laser to decompose adsorbed triisobutyl aluminum (TIBA) vapors. The laser was then switched off, and the reaction was observed to be self sustaining in the pre-nucleated areas while the entire substrate was heated.⁵² Variations on this technique have been explored using focused ion beams to damage a silicon surface exposed to vapors of $\text{Fe}(\text{CO})_5$ or TIBA. Deposition of the respective iron and aluminum films was also self sustaining after ion bombardment was stopped.⁵⁸

A CVD reaction is generally catagorized in terms of the pressure range used during the reaction.⁵⁹ Thus, as the names imply, atmospheric pressure CVD (commonly called APCVD) and low pressure CVD (LPCVD) are the common types. Both of these are further classified by the reactor type as either hot wall or cold wall. APCVD reactors were the first to be used commercially.^{60,61} Operation at atmospheric pressure allows for simple system design and for high film deposition rates. These reactor systems suffer, though, from increased homogeneous gas phase reaction and poor step (feature) coverage. Since these reactors are operated in a mass transport limited regime, the reactant flux to all

parts of every substrate must be precisely controlled for uniform coverages. This places severe constraints on reactor geometry and on gas flow patterns.

LPCVD reactors normally operate at pressures below about 2 torr, and film depositions are generally in the reaction rate limited regime. These systems overcome problems of nonuniformity, step coverage, and particulate contamination limitations of the APCVD apparatus.^{62,63,64} At reduced pressure the diffusivity of reactant gas molecules is sufficiently increased that mass transfer to the substrate no longer limits film growth. The elimination of mass transfer constraints on reactor design allows for high substrate capacity as well as increased step coverage and uniformity. The low pressure operation also reduces homogeneous nucleation in the gas phase which is the primary source of particulate contamination.

Hot wall and cold wall reactors are so named from the method of substrate heating. Hot wall reactors normally employ radiant heating from outside the reactor and thus films form on the inside of the heated reactor walls as well as on the substrate. These systems suffer from low throughput, poor uniformity, and particulate contamination; they find little use in modern film deposition. Cold wall reactors use infrared heating or radio frequency heating of a substrate susceptor or (especially for laboratory scale systems) an internal resistively heated substrate stage to control substrate temperature. These types of reactors are

most common in modern production and research settings. Special commercial designs allow for high throughput from continuous conveyor belt substrate introduction systems. Cold wall reactors are largely free from the particulate and uniformity problems associated with hot wall systems.

The present work describes the development of a selective gold CVD process and some study of its chemistry relating to the selectivity. This section explored the need for the research described here along with a brief introduction to the development and methods of CVD. In the next chapter the chemistry and physics of CVD are discussed with emphasis on the current thinking in terms of how one physically differentiates surfaces for the achievement of selectivity during thin film deposition.

CHAPTER II PHYSICAL AND CHEMICAL ASPECTS OF CVD AND SELECTIVITY

In a typical CVD process various sequential reaction steps occur:^{65,66}

- 1) free or forced convective transport of the gaseous reactants to the boundary layer surrounding the substrate
- 2) diffusive or convective transport of the reactants across the boundary layer to the surface of the substrate
- 3) adsorption of the reactants on the surface of the substrate
- 4) chemical reactions (surface reactions) between adsorbed reactants, between adsorbed reactants and reactants in the vapor and/or between reactants in the vapor
- 5) nucleation
- 6) desorption of some of the reaction products from the surface of the substrate
- 7) transport of the reaction products across the boundary layer to the bulk of the gas mixture
- 8) transport of the reaction products away from the boundary layer

Even though any of these steps may be rate limiting, only three main categories of process control are normally important:

- 1) thermodynamic control
- 2) surface kinetics control
- 3) nucleation control

Thermodynamic control means that the deposition rate is equal to the mass input rate into the reactor which occurs under extreme conditions (very high reactant flow rates, high temperatures etc.). Kinetic control occurs if the deposition rate is lower than the mass input rate into the reactor or across the boundary layer. Nucleation control is achieved at low supersaturation of the reactant vapor.

The initial stages of thin film growth are often impeded by the presence of a nucleation barrier. Control of this nucleation barrier is the most important consideration in terms of promoting area selective thin film growth by CVD.^{67,68,69} Results from the present work support that conclusion. It is convenient to classify nucleation barriers as being either due principally to physical or to chemical effects. In the following sections the processes relevant to CVD prior to nucleation are first discussed followed by treatments of the two nucleation types.

Pre-nucleation Processes

All practical theories of thin film nucleation have as an initial step the impingement of vapor molecules on the

surface.⁷⁰ After impingement, the vapor molecules can either adsorb and stick permanently, adsorb and re-evaporate or simply bounce off the surface with negligible residence time. Vapor molecules which impinge on the surface exchange energy with the condensed phase by means of interactions with atoms, groups of atoms or the lattice. These interactions in time result in thermal equilibration in accordance with thermodynamic principles unless the vapor molecule re-evaporates or rebounds prematurely. In the latter case, the thermal accommodation coefficient, defined as

$$\alpha_T = \frac{E_v - E_r}{E_v - E} = \frac{T_v - T_r}{T_v - T} \quad \text{II.1}$$

will be less than unity. Here E_v is the incident kinetic energy, E_r is the energy of the desorbed atom before equilibration with the surface and E is the energy of the desorbed atom after it has equilibrated with the surface and T_v , T_r and T are the corresponding temperatures. Measurement of α_T yields information on the degree of energy transfer with the surface. T_v is obtained by measuring the temperature of the gas source which allows for the direct determination of the average gas velocity. The degree of energy transfer is measured by accurately determining the change in surface temperature as the gas is admitted. The nature of energy transfer processes are studied in terms of the

translational, vibrational, and rotational gas energy transfer with the vibrational states of the surface.^{71,72,73}

As can be seen from II.1, accommodation is very inefficient if T_r approaches T . Goodman⁷⁴ has estimated that thermal accommodation is essentially complete if E_v is smaller than E . For typical activation energies of the order of 0.5 eV, incident molecules would have to arrive with translational energies associated with temperatures in excess of 6000°C before thermal accommodation would be incomplete. Lennard-Jones⁷⁵ has estimated the time necessary for an incident species to lose all of its excess kinetic energy and to accommodate thermally to be of the order of $2/v$ where v is a characteristic frequency of the substrate lattice vibrations. Thus, incident atoms will lose all of their excess kinetic energy within a few lattice oscillations and except for species with very high translational energies, all species can be assumed to equilibrate thermally with the surface immediately.

Once adsorbed species have reached a certain population density a steady state will result, in the absence of nucleation, for which the incident and evaporating fluxes are equal. Substrate coverage then becomes a function of the incident flux rate R from

$$n_1 = \frac{R}{v_0} \exp\left(\frac{\Delta G_{des}}{kT}\right) \quad \text{II.2}$$

where v_0 is the desorption attempt frequency which is essentially a molecular vibrational frequency and ΔG_{des} is the free activation energy for the desorption process. If the vapor source is turned off and R approaches 0, the coverage of adsorbed species becomes 0. The mean residence time of an adsorbed species is then given by

$$\tau_a = \frac{1}{v_0} \exp\left(\frac{\Delta G_{des}}{kT}\right) \quad \text{II.3}$$

Thus a stable condensation may not be possible even if the supersaturation ratio (the ratio of incident vapor flux to the flux of species from the surface bulk) for nucleation is much larger than unity.

At some vapor flux level and due to surface migration and collision of equilibrated species, a somewhat stable surface aggregate whose members are bound by the condensation energy will form for which the probability of decomposition of the molecular species will be greatly increased due to the increased residence time. To be sure, at sufficiently high surface temperatures and given that thermal accommodation of nearly all arriving species is complete, decomposition of single molecules will become complete.

Physical Barriers to Nucleation

Even though surface aggregates are more stable than adsorbed monomers due to the condensation energy, this stabilization will diminish as the aggregate grows due to

the high surface tension resulting from the high surface to volume ratio. According to a modification for surfaces of the capillarity model of Volmer and Weber⁷⁶ and Becker and Doering,⁷⁷ positive free energy fluctuations are necessary to form stable aggregates of the condensed phase which in turn introduces the necessity of overcoming a nucleation or activation barrier. Because of this barrier a super-saturation ratio greater than unity is required for nucleation to occur. The growing aggregate thus goes through a maximum in free energy (minimum stability). This energy maximum corresponds to an aggregate of critical radius R^* .

The critical radius can be calculated from free energy considerations by assuming aggregates of surface area $a_1 r^2$ and volume $a_2 r^3$ and a contact area between the aggregate and surface of $a_3 r^2$ where the a 's are constants and r is the mean radius of the aggregates. The total free energy of the aggregate with respect to dissociation into the vapor phase and as a function of radius is given by

$$\Delta G = a_2 r^3 \Delta G_v + a_1 r^2 \sigma_{v-c} + a_3 r^2 \sigma_{s-c} - a_3 r^2 \sigma_{s-v} \quad \text{II.4}$$

Here ΔG_v is the free energy of condensation of the bulk film material and is given by

$$\Delta G_v = \frac{kT}{V} \ln \frac{R}{R_\theta(b)} \quad \text{II.5}$$

σ_{v-c} and σ_{s-c} are the surface and substrate/deposit interfacial free energies of the aggregate, respectfully, and σ_{s-v} is the surface energy of the substrate. The volume of one molecule of condensate is V and $R_0(b)$ is the evaporation rate of monomers from the bulk at the substrate temperature. The ratio $R/R_0(b)$ is the supersaturation ratio. Differentiating IV.4 with respect to aggregate size, r , yields

$$\frac{\partial \Delta G}{\partial r} = 3a_2 r^2 \Delta G_v + 2a_1 r \sigma_{v-c} + 2a_3 r \sigma_{s-c} - 2a_3 r \sigma_{s-v} \quad \text{II.6}$$

It is assumed here that aggregate shape and free energy values do not change with size.

The free energy of the aggregate is a maximum for an aggregate of critical size, r^* . Thus, setting $\partial \Delta G / \partial r = 0$ from the previous relation r^* becomes

$$r^* = \frac{-2(a_1 \sigma_{v-c} + a_3 \sigma_{s-c} - a_3 \sigma_{s-v})}{3a_2 \Delta G_v} \quad \text{II.7}$$

and the free energy of an aggregate of critical radius r^* is given by

$$\Delta G^* = \frac{4(a_1 \sigma_{v-c} + a_3 \sigma_{s-c} - a_3 \sigma_{s-v})^3}{27a_2^3 \Delta G_v^2} \quad \text{II.8}$$

This maximum in aggregate free energy corresponds to a minimum in aggregate stability and thus represents the energy barrier toward the formation of a stable nucleus. In terms of selective MOCVD this free energy barrier could be

used to advantage for inhibiting growth on desired surfaces since the maximum driving force for desorption would occur in aggregates of critical size.

Chemical Barriers to Nucleation

While physical nucleation barriers result from the equilibrium thermodynamics of the carrier substrate interactions, chemical barriers result from kinetic factors. Since surface catalyzed reactions are chemically complex, an analogous relation to IV.8 cannot be written for a critical free energy barrier. If the overall process is surface sensitive, however, it can be assumed that a surface reaction must be rate limiting or

$$k_n = v_n \theta_n \exp\left(-\frac{\Delta G_n}{kT}\right) \quad \text{II.9}$$

Here ΔG_n is not the free energy for the attainment of a critical cluster size, but the barrier for a chemical initiated reaction. The barrier jump attempt frequency and surface coverage are given by v_n and θ_n respectively. All vapor species in the vicinity of a surface experience an attractive potential⁷⁸ which, for the promotion of surface reactions, should fall in the range of chemisorption energies (i.e. 8-10 eV versus about 0.25 eV for physisorption). Thus, chemical reaction barriers can be most easily surmounted on surface defect sites, chemical impurities (desirable and undesirable), dangling surface bonds, grain bound-

aries, grain edges, or any other high free energy attribute. Practically, surfaces can be modified by damaging desired areas to promote carrier decomposition, or patterned films of high catalytic activity can be deposited on surfaces which have a high critical nucleation free energy in order to promote selective MOCVD.

CHAPTER III EXPERIMENTAL APPARATUS AND MATERIALS

The scope of this study was limited to the investigation of the decomposition characteristics and resulting thin film properties of a single volatile gold carrier, triethyl phosphine gold chloride, and its interactions with surfaces of silicon that had been micropatterned with thin films of tungsten. Since the motivation for this work grew from interests in problems associated with integrated circuit fabrication, and due to the lack of a suitable processing environment for the production of viable test circuits, emphasis was placed on developing and studying the chemistry of a gold on tungsten selective deposition scheme which might later be perfected and integrated into existing industrial processing environments. The study consisted of three main parts: 1) development of a selective gold on tungsten patterned on silicon MOCVD scheme, 2) identification of the optimum deposition parameters, and 3) temperature programmed desorption study of the chemistry of the gold carrier interaction with surfaces of silicon and surfaces of tungsten. This chapter describes all apparatus and instrumentation used in the development and study of the selective CVD of gold.

Apparatus and Instrumentation

Five different systems of apparatus and their associated instrumentation were developed and assembled for use in selective gold CVD studies. These were:

- 1) candidate gold carrier compound test ampule and system,
- 2) pulsed radio frequency MOCVD reactor, instrumentation, and vacuum system,
- 3) catalytic differentiation MOCVD reactor and vacuum system,
- 4) system for study of optimum deposition parameters,
- 5) thermal desorption mass spectroscopy vacuum system, reactor, and instrumentation.

Development, construction, and assembly of each is discussed in detail below. Operational procedures are described in Chapter IV.

Candidate Gold Carrier Identification Test Ampule and System

Candidate compounds were subjected to qualitative tests of their behavior under conditions that were anticipated in planned experiments on selectivity. To facilitate these tests, a simple system for differentially heating the compound and substrate in vacuo was devised. The test system included a vacuum sealed glass ampule containing the candidate carrier compound and a tungsten substrate, a heating system for the control and monitoring of candidate compound temperature, and a laser for the heating of the

tungsten substrate. Figure III.1 is a block diagram of the experimental arrangement.

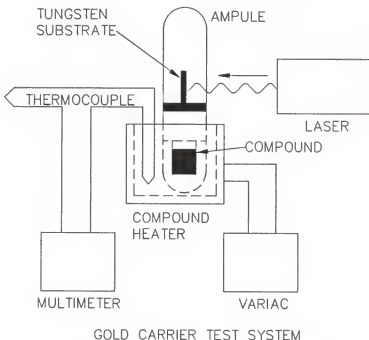


Figure III.1. Block diagram of carrier compound test system

Vacuum sealed ampule construction.

The vacuum sealed ampule is illustrated in Figure III.2. It was custom fabricated by inserting a snug fitting sleeve of 0.16 in. i.d. thick wall borosilicate glass tubing about 0.5 in. into another approximately 4 in. long piece of 0.4 in. o.d. borosilicate glass tubing. The two pieces were fused together by heating with a gas flame aimed at the insertion point, then the excess thick wall tubing was pulled off before the glass solidified. Further heating of the same region left a sealed rounded end containing a small

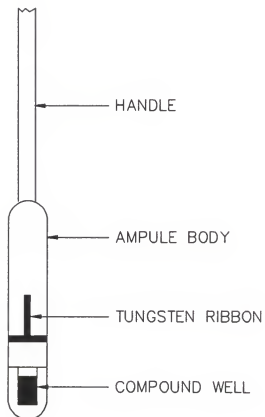


Figure III.2. Diagram of assembled vacuum sealed ampule.

well for holding the candidate carrier compound. Once the end was formed and cooled, candidate gold carrier compound was placed in the well by packing a small amount of compound in another long piece of the 0.16 in. i.d. thick walled tubing and inserting this into the ampule in such a manner that the inserted tube seated against the top of the well. Compound was then introduced into the well by pushing a 0.16 in. dia. glass rod through the inserted tubing in such a way that the compound was forced ahead of the rod and into the well. A 1 in. long piece of 0.01 in. thick and 0.08 in.

wide tungsten ribbon was bent into a semicircle of slightly larger diameter than the i.d. of the ampule and then bent further such that a straight section about 0.5 in. long extended from and perpendicular to the semicircle's center. The slightly larger size of the formed semicircle produced a spring action that held the tungsten sample in place when compressed and slid into the ampule. This was done such that the straight section pointed toward the open end of the ampule and the semicircle rested about 0.5 in. above the top of the compound well. Once the compound and tungsten sample had been introduced into the ampule, the ampule was then fused to a glass side arm which mated to a valved O-ring quick couple attached to an oil diffusion pumped and liquid nitrogen trapped glass vacuum system. Once the ampule was sealed to the side arm and the side arm attached to the vacuum system, the ampule was exposed to the vacuum and the system was pumped until a pressure of about 1×10^{-5} torr was reached as indicated by a Mcleod gauge. The ampule was then removed from the side arm by carefully and uniformly heating the ampule with a gas torch flame near the seal to the side arm while pulling on the bottom of the ampule. Atmospheric pressure thus tended to collapse the tubing upon itself, and the pulling produced a fine thread capillary between the ampule and the side arm. At this point, the torch flame was increased in intensity and aimed at the narrowest point of the capillary which caused the ampule to separate from the side arm and form a small ball of glass at

the separated ends of the capillary thus sealing both the ampule and the vacuum system against the atmosphere. The remaining capillary extending from the ampule was incorporated into the top of the ampule by heating from the end of the capillary and following the growing ball of glass back to the body of the ampule and finally heating carefully such that the ball was melded into a rounded end at the top of the ampule and the vacuum inside the ampule was maintained. Finally, an 8 in. long piece of glass rod was fused to the ampule for use as a handle.

Compound heating system

A silicon oil heating well bath was formed by rounding one end of a 1 in. long and 1 in. dia. piece of aluminum rod such that it fit snugly and matched the contour of the heating surface of a 50 milliliter round bottom flask heating mantle. Power to the mantle was controlled with a Variac auto transformer. A 0.563 in. diameter and approximately 0.563 in. deep blind hole was centered and drilled into the end opposite the rounded portion for containment of high temperature silicon oil and for placement of a thermocouple and the compound containing end of the ampule. A type E thermocouple with a 0°C reference connected to a Keithly 177 Microvolt digital multimeter was used to monitor the compound temperature.

Laser system description.

A 5 watt Spectra Physics model 265 argon ion laser was used to heat the tungsten ribbon sample. When the unfocused

laser light was made incident onto the straight portion of the tungsten ribbon inside the evacuated ampule, the ribbon glowed red hot at the point of incidence.

Pulsed Radio Frequency MOCVD Reaction System

The pulsed radio frequency MOCVD reaction system was composed of two sub-systems:

- 1) the pulsed radio frequency power generation system
- 2) the MOCVD reactor

Each subsystem is described in detail below. Figure III.3 is a schematic of the reaction system.

Pulsed radio frequency power generation system

The pulsed radio frequency power generation system was comprised of a radio frequency source, an RF amplifier, an RF matchbox circuit, and a pulse generator circuit.

Radio frequency source. An Icom 701 radio transceiver, capable of producing 100 watts forward power and tunable over the range of 1 to 30 megahertz was used for primary RF power generation.

Radio frequency amplifier. An Amitron model AL-80A RF amplifier allowed for the production of 1000 watts forward power when connected to the RF source. Power from the RF generator was supplied by a heavy coaxial cable.

Matchbox circuit. The matchbox circuit was based on a design described elsewhere.⁷⁹ The two high current carrying plates were constructed from 0.75 in. copper plate which was drilled and channeled for water circulation. Two

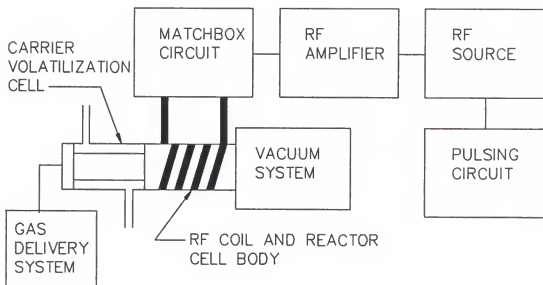


Figure III.3. Block diagram of pulsed RF MOCVD reaction system.

grounding plates were constructed from 0.25 in. copper plate and were soldered together in an "L" shape for mounting of the variable vacuum capacitors. The high voltage side of the variable capacitors communicated with the current carrying plates through custom made 0.063 in. copper straps. These straps were attached to the vacuum capacitors with hose clamps. A 1 in. dia. inductor coil was constructed from 0.125 in. copper refrigeration tubing, and one end was soldered to one of two water channel ports in each of the current carrying plates. Typically, the coil was first wrapped around the reactor cell body (described below) before soldering to the plates. The other water port in each plate served as either an inlet or outlet for the cooling water circulation. Power was supplied through a

heavy coaxial cable attached to the matching circuit at the ground plate and the high capacitance side of the induction coil.

Pulsing circuit. The pulsing circuit consisted of a Hewlett Packard model 8002a function (pulse) generator to control a custom built switching circuit which actuated the on and off keying of the RF primary generator. Pulse width and frequency were measured with a Transistor Specialties model 361R timer/counter. Minimum full power pulse widths of 3 millisecond were routinely obtained at a maximum useable frequency of 50 hertz.

Pulsed RF MOCVD Reactor

The pulsed RF MOCVD reactor is composed of the reactor cell assembly and the reactor vacuum system.

Reactor cell assembly. The reactor cell assembly is illustrated in Figure III.4. It is composed of a brass valve feedthrough, a glass water jacketed carrier compound volatilization cell, and the reactor chamber. The custom blown glass water jacketed volatilization cell measured about 3 in. long and was constructed from two #25 Pyrex O-Ring joint tubes. One end of the cell channel (inside the tube) was necked down to about 0.25 in. dia. while the opposite flange end was unobstructed. Hot water for compound volatilization was supplied by a Haake Type F circulator/heating bath connected to the cell with plastic tubing and valved on the pump side for rapid introduction of hot water at the beginning of an experimental trial. The

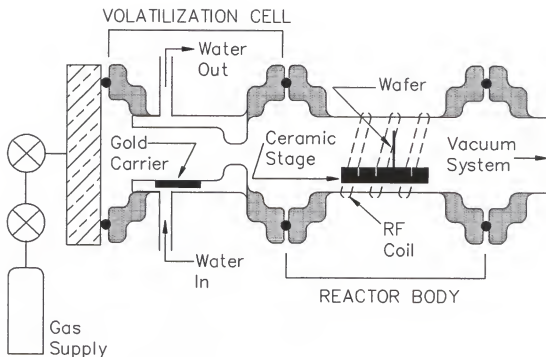


Figure III.4. Diagram of RF MOCVD reactor.

reactor chamber was constructed, likewise, from two #25 Pyrex O-Ring tubes and also measured about 3 in. in length. It contained a rectangular machined Maycor ceramic block which was slotted so as to hold the substrate wafer surface perpendicular to the bore of the tube. The matchbox circuit inductor was closely wrapped around the outside of the cell. The reactor body was joined to the necked down end of the volatilization cell through an O-ring and secured with an O-ring tube clamp. The opposite end of the volatilization cell was joined to a brass valve assembly through a brass flange custom machined to accommodate a face seal with the O-ring for the #25 joint. The valve assembly itself consisted of a brass, O-ring sealed high conductance valve

attached on one end to an in house fabricated micro metering flow valve. The other end of the high conductance valve communicated with the reactor cell through the brass flange. These were joined by brazing. The other end of the reactor cell body was mated with the vacuum system through an O-ring to another #25 O-ring tube.

Vacuum system. The vacuum system consisted of a Spedivac model E04 oil diffusion pump backed by a Sargent Welch model 1380 two stage oil mechanical pump. The diffusion pump was fitted with a liquid nitrogen Misner type trap. The entire pumping stack communicated with an 18 inch bell jar through a 6 in. butterfly valve. One port of the bell jar support ring was fitted with an ionization pressure gauge while another port contained a thermocouple type pressure transducer. A third port was fitted with a custom machined brass ball valve assembly. The ball valve controlled vacuum communication between the bell jar and the MOCVD reactor. A glass to metal seal was soldered on the metal end to the brass valve assembly. The other end was fused to the #25 O-ring joint for attachment to the reactor cell body. The reactor side of the valve assembly contained three additional ports, one port for communication with a liquid nitrogen trapped mechanical pump used for rough pumping the reactor, another port fitted with an O-ring quick couple for the mounting of a Baratron model 220BA pressure transducer, and finally a threaded port for accommodation of a thermocouple type pressure transducer.

Selectivity From Catalytic Activity Differences Apparatus

The apparatus for these experiments was identical to that used for the RF tests except for modifications to the reactor body assembly. In addition the RF system was eliminated from the experimental set up.

Reactor body assembly. The adapted reactor body assembly used in the RF studies described in the previous section is illustrated in Figure III.5 and was modified as follows. A 0.375 in. o.d. and 2 in. long piece of glass tubing was attached to the pumping end of the tube about 0.5 in. from the O-ring joint. This tube accommodated a custom machined brass electrical feedthrough chamber for introduction of power and thermocouple lines. The feedthrough chamber assembly was connected to the reactor body through an O-ring quick couple. The chamber was sealed with an O-ring face seal feedthrough flange that had a ceramic thermocouple feedthrough and a 6 line solder post ceramic electrical feedthrough soldered in a machined hole in the flange face. Power was fed to a machined maycor heater plate through number 14 multistranded teflon coated wire. The heater plate measured approximately 1 in. long and 0.625 in. wide and 0.25 in. thick. Two 0.125 in. holes were drilled lengthwise centered about 0.187 in. from either edge and midway between the major faces. One end contained a milled channel measuring 0.187 in. deep and connected the drilled holes. Nicrome wire measuring 0.013 inch in diameter was

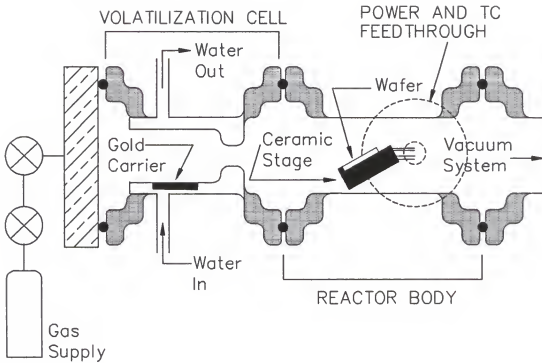


Figure III.5. Diagram of catalytic differentiation MOCVD reactor.

tightly wound into a slightly less than 0.125 in. diameter coil measuring about 2.5 in. long. The filament coil was filled with a slurry of high temperature potable ceramic, and then each end was inserted evenly into a drilled hole from the channeled end thus forming a "U" shape when set into place by pulling each end through the holes. The bottom of the "U" occupied the milled channel. Once the filament was pulled into place, any remaining voids in the drilled and machined regions were filled with ceramic slurry then the heater was baked at 150°C for about 1 hour to set the ceramic. Excess coil extending from the two holes was unwound and trimmed back to about 1 inch for use as power

connections. Another 0.125 in. 0.5 in. deep blind hole was drilled centrally into the end opposite the channel and midway between all edges for insertion of a 0.125 in. copper tube that contained a type E thermocouple. Thermocouple leads inside the reactor were insulated with narrow gauge teflon tubing. The heater also was drilled and tapped for a #4-36 screw that intersected the thermocouple hole. It secured the thermocouple and acted as an elevation support for the back end of the heater. The heater thus rested inside the reactor on three points: the front two lower corners and the head of the screw. The face pointed toward the volatilization cell end making about a 30 degree angle with the center bore of the tube. Finally, a narrow ledge was machined on the front of the heater to keep wafers from sliding off the device. Power to the heater was controlled with a Variac auto transformer. The resistivity of the filament measured approximately 10 ohms, thus for 50 volts applied from the variac the heater produced 250 watts.

Apparatus for Optimum Deposition Parameters Identification

Studies of the catalytic differentiation of the silicon and tungsten surfaces indicated that the compound vapor pressure and wafer temperature were the primary deposition variables. Furthermore, it was found that a relatively narrow parameter window existed for the successful performance of selective depositions. To explore this further an experimental system was designed and constructed to allow

for much finer control over these variables relative to that which had been achieved in apparatus used in selective gold MOCVD studies to this point. The entire reactor system was constructed from glass and metal so as to allow for the heating of the entire assembly in an oven and thus achieve better definition of the gold carrier vapor pressure. Utilization of a fine gauge wire thermocouple allowed improved control and knowledge of the substrate temperature. Figure III.6 is a diagram of the system.

A glass reactor vessel was constructed from a 2 liter Pyrex round bottomed flask. The neck of the flask was attached to a custom machined Housekeeper type glass to stainless steel seal. The metal end of the seal was welded to a 2.75 in. dia. Conflat type high vacuum flange which had been drilled and machined for accommodation of the metal part of the seal. In the imaginary plane that divides the flask into hemispheres and parallel to the Conflat flange, a hole was blown into the flask and a 0.5 in. long and 0.375 in. i.d. glass tube was attached radially to the flask. A 1 in. dia. glass ball was then blown in such a manner that it symmetrically enveloped the tube and sealed the reactor by sharing a common seal with the tube and the reactor body. This cavity served as the carrier compound reservoir. Another 2.75 in. dia. Conflat flange was drilled for accommodation of 5 weldable ceramic insulated electrical feed-throughs. Two of these were used for the introduction of power to the wafer heater and two others for thermocouple

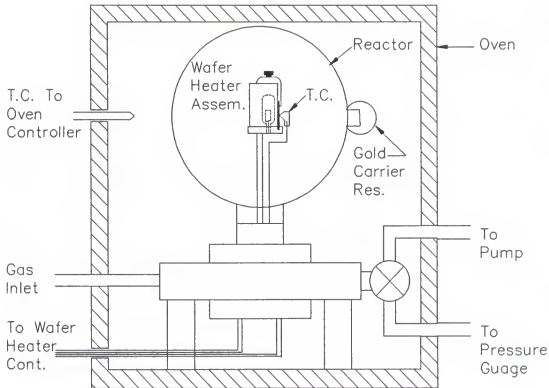


Figure III.6. Diagram of MOCVD reactor system used in selectivity optimization studies.

connections. The other feedthrough supported a steel wire which was used for placement and maintenance of the thermocouple at the wafer's surface.

An approximately eight inch long and 0.25 in. dia. steel rod was welded into a 0.25 in. i.d. hole that was centered and drilled perpendicular to the flange face on the knife edge side of the flange. This rod supported the wafer heater which is illustrated in Figure III.7. Figure III.8 illustrates various views of the heater assembly body sections. The middle section of the three piece 304 stainless steel wafer heater/support assembly was machined from 3/4 inch rod. A 0.5 in.dia. hole was drilled off center

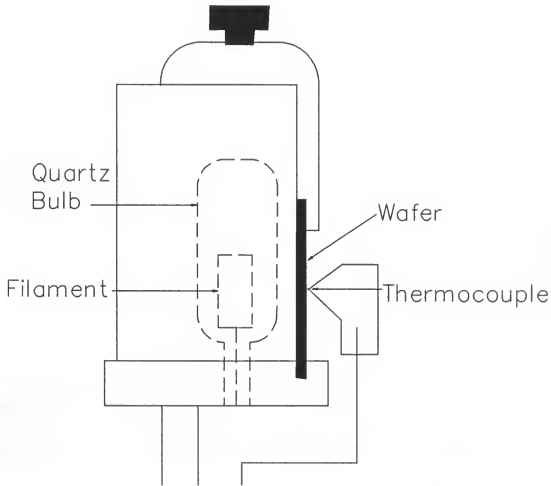


Figure III.7. Enlargement of wafer heater assembly.

through the length of the rod so that an approximately 0.375 in. wide channel was opened in the side of the rod. This piece rested on the bottom section which was a disc of stainless steel and also supported the quartz projector lamp. The top portion of the wafer heater/support was constructed by hollowing a 0.5 in. dia. rod slightly larger than the diameter of the projector lamp such that it fit into the hole drilled in the middle section. Grooves were machined into the bottom and top portions of the heater

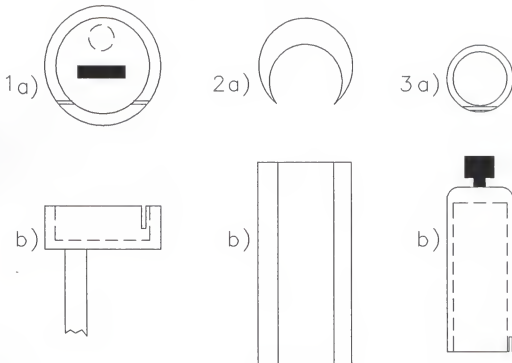


Figure III.8. Various views of wafer heater assembly.
 1 a) Top View of bottom section.
 b) Side view of bottom section.
 2 a) Top view of middle section.
 b) Front view of middle section.
 3 a) Bottom view of top section.
 b) Side view of top section.

assembly for placement of the substrate wafer which was held in place by gravity when the top portion was slid into the middle section. The back side of the wafer was exposed in a line of sight to the lamp filament.

Both conflat flanges mounted to a custom designed 304 stainless steel plate measuring about 7 in. square and 0.75 in. thick. Conflat flange knife edges were machined in the center of both faces around a 1.2 in. dia. hole that was drilled for passage of the heater assembly. The plate was

drilled and tapped on both sides to accommodate 1 in. long 1/4 in. #28 threaded rods for the mounting and securing the flanges. Two holes were drilled into opposing ends and midway from either edge of the plate such that they intersected the diameter of the face hole. One of these had a 0.125 in. dia. stainless steel tube brazed into it for introduction of gasses into the reactor. The other accommodated an all metal high vacuum valve which brazed directly to the plate. Four approximately 7 in. long 1 in. dia. aluminum rods were bolted to holes drilled on each corner of the plate for support of the entire reactor assembly.

The entire reactor resided in a 3600 watt general purpose laboratory oven. Holes were drilled into the oven wall for passage of the 0.125 in. dia. stainless steel gas tubing and for the introduction of two lengths of 3/8 in. dia. copper refrigeration tubing. Both of these lengths of tubing were brazed to a copper "T" fitting inside of the oven which was in turn brazed to the exit port of the all metal valve in the reactor support plate. One of these tubes allowed for communication between the reactor (through the all metal valve) and a Baratron model 220BA pressure transducer. The other length connected the reactor to a Sargent Welch two stage oil mechanical vacuum pump. This second piece of tubing also contained a coil winding which resided in a liquid nitrogen dewar flask for use as a trap. A type J thermocouple was mounted inside the oven near the reactor bulb to monitor and control the oven temperature.

The thermocouple was attached to a Watlow temperature controller which actuated the oven relays. Another Watlow controller sensed the thermocouple mounted on the wafer surface and regulated power to the lamp wafer heater from a Variac power supply.

Thermal Desorption Mass Spectroscopy (TDMS) System

The TDMS system was composed of three subsystems:

- 1) the vacuum console,
- 2) the mass spectrometer computer control system
- 3) the substrate and carrier compound heating systems.

Each component is described in detail below.

The vacuum console

The vacuum console was composed of the mass spectrometer quadrupole chamber, the TDMS chamber and the pumping system.

The mass spectrometer quadrupole chamber. The mass spectrometer quadrupole chamber was a modified Finigan Model 3200/3300 quadrupole mass analyzer housing. The original chamber came equipped with an O-ring flange for the attachment of a liquid nitrogen trapped diffusion pump stack. This pumping system allowed for the attainment of vacuum of the order of 1×10^{-7} torr and produced a strong hydrocarbon background pattern; both of these features were unacceptable for the surface analysis studies described in this section. To overcome these limitations the chamber was modified by replacing this flange with a 10 in. dia. Conflat flange

which was welded to the chamber in its place. This flange allowed for the attachment of a turbomolecular pump which is described below. Two working ports were provided with the original chamber and these were employed unmodified. One port was sealed with a 3 in. dia. Viton O-ring and flange fitted with a Vernier dial controlled ultra high vacuum variable leak valve which was used primarily for back filling the vacuum system. The other working flange was a 2.75 in. dia. conflat type and was used for attachment of the TDMS chamber.

The TDMS chamber. The TDMS chamber consisted of the chamber body, the substrate mounting flange, and the liquid nitrogen cooled substrate isolation trap system. The chamber body was machined from 304 stainless steel. The top and bottom of the chamber supported smooth faced flanges for the mounting of the O-ring sealed substrate mounting and isolation flanges. Three flange supports were welded to the side of the chamber midway between the top and bottom such that each flange center line was contained in the same plane and parallel to the faces of the top and bottom flange. One support contained the 2.75 in. dia. Conflat flange for mounting the chamber to the mass spectrometer chamber. At a 90 degree angle to the conflat flange, a smooth faced flange for the placement of the O-ring sealed carrier volatilization and beam production cell (described below) was attached. At angles of 135 degrees to both of the two other flanges was attached an O-ring grooved flange for the

mounting of a quartz window for introduction of laser light for heating the backside of the substrate. Figure III.9 is a top view schematic of the chamber body.

The substrate support flange is illustrated in Figure III.10. It was machined from 304 stainless steel and contained an O-ring groove for sealing when mounted to the TDMS chamber bottom. The substrate supports consisted of two 0.25 in. dia. stainless steel tubes each cross drilled with two 0.125 in. dia. holes one near the top and the

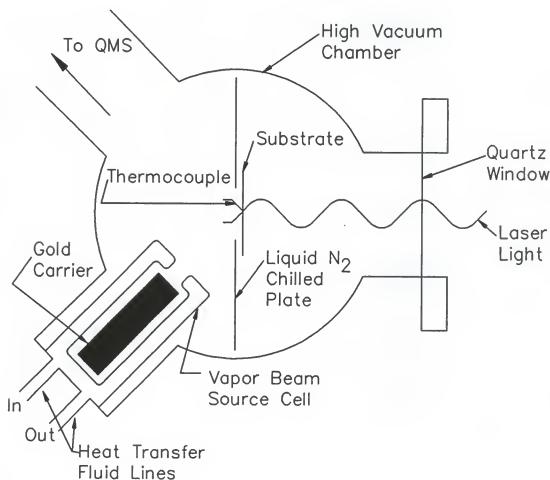


Figure III.9. Top view through TDMS reactor cross section.

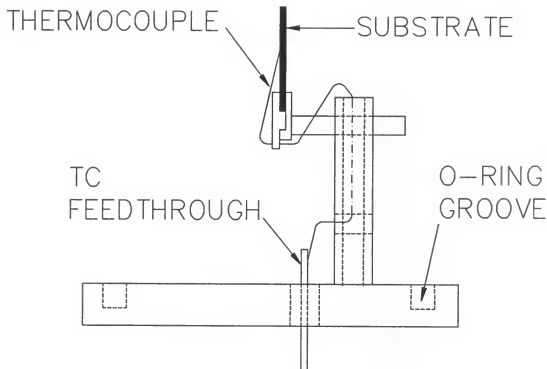


Figure III.10. Diagram of TPD wafer holder flange assembly.

another about 0.375 in. from the other end. The holes nearest the rod ends allowed passage of 0.125 in. dia. stainless steel rods which were attached to the substrate holder. The substrate holder was machined from two pieces of stainless steel and was designed to support the substrate with minimal contact area thereby providing minimal heat sink. The holder contained two 0.0013 in. dia. holes for holding a fine wire thermocouple for positioning against the wafer surface. Each thermocouple lead was threaded through one hole and then through a hollow of the 0.25 in. dia. rods and exited at the 0.125 in. dia. hole 0.375 in. from the rod

end. Each 0.25 in. dia. rod was held perpendicular to the flange when slipped into 0.25 in. diam 0.25 in. deep reamed holes in the vacuum side face. The thermocouple ends were spot welded to separate conductors of an electrical feed-through welded into the support flange. When the wafer support flange was assembled and mounted on the TDMS chamber with a substrate in place, the back of the substrate was centered on the center line of the quartz window port, and the face was coincident with the TDMS chamber diameter and parallel to the flange face.

The liquid nitrogen trap substrate isolation system is illustrated in Figure III.11. The inner and outer tubes were sized from thin wall stainless steel. These were each welded to a doughnut shaped ring at the top and the outside tube was welded to another doughnut shaped ring which contained an O-ring for sealing against the TDMS chamber top flange. A copper disc was brazed to the bottom of the inner tube forming the vacuum tight trap. A square copper bar was attached with screws to the copper disc such that one perpendicular face coincided with the diameter of the disc. Attached to this face was a 0.015 in. thick piece of hard copper plate which had a 0.400 in. dia. hole drilled in its center. Its length and width were such that when the entire TDMS system was assembled the plate edges were about 0.015 in. from the walls and bottom of the chamber's inside surface, and the hole exposed the substrate surface to the side of the chamber containing the carrier cell and mass

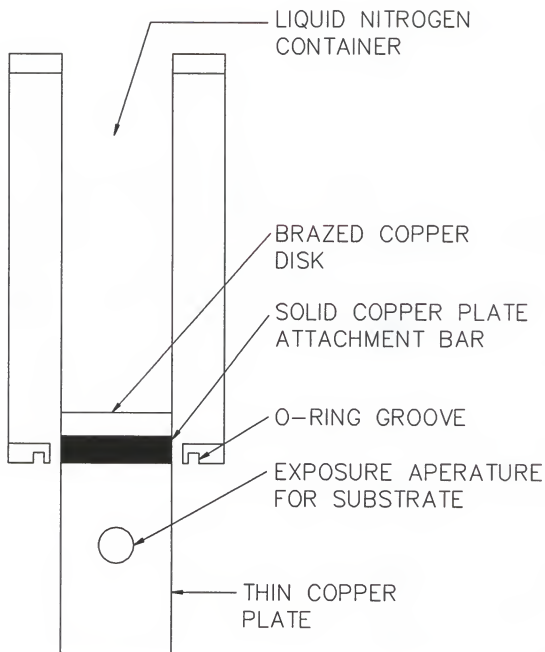


Figure III.11. TPD wafer isolator cold-finger trap assembly.

spectrometer ports. The plate thus acted as a cold surface to trap any stray carrier which was not incident on the substrate's surface.

The vacuum system. The quadrupole and TDMS chambers were pumped with a Leybold-Heraeus Turbovac 560M turbo molecular pump which was mounted to the above mentioned 10 in. dia. Conflat flange that was welded to the quadrupole chamber. The turbomolecular pump was backed by a Sargent Welch high capacity two stage oil mechanical pump. Pressure measurements were made with an ionization pressure gauge mounted on the quadrupole chamber near the throat to the turbomolecular pump. Typical pressures of 5×10^{-9} torr were attainable after bake out of the vacuum system.

The computer controlled mass spectrometer electronics system

The Finigan Model 3300 mass spectrometer control and output systems were operated and monitored respectively with an IBM Personal Computer Data Acquisition and Control Adapter with 2 programmable digital to analog and 4 analog to digital output and input channels. The data acquisition adapter was installed in a PC-XT type clone computer equipped with a 30 megabyte hard disc drive to store programs and data. All data acquisition and control programs as well as data manipulation programs used in post experiment processing were written in the C programming language (program listings are given in Appendix A). All data acquisition adapter input and output channels were of 12 bit resolution. The 0 to 800 atomic mass unit full scale range of the mass spectrometer was controlled with a 0 to 10 volt ramp from a digital to analog channel of the control adapter. The 0 to 10 volt full scale output of the mass spectrometer was monitored

with a channel of identical full scale capacity on the data acquisition adapter. The spectrometer output system was equipped with a 5, 10 50, and 100 gain amplifier to boost signal intensity if needed. Another input channel monitored the 0 to 2 volt full scale analog output signal from a Keithly 177 Microvolt digital multimeter which measured the emf of the substrate thermocouple.

Substrate and carrier compound heating system

The substrate heating system employed the same argon ion laser described in the carrier compound identification system. When heating the wafer, the beam was passed through an approximately 10 inch focal length double convex lens that was placed between the laser and the wafer such that the incident area of the beam was maximized on the wafer. This was done to distribute heating evenly avoiding any hot spots on the wafer front surface.

The carrier heating system consisted of a glass Knudsen type cell similar to the one used in the RF and initial catalytic MOCVD experiments. It was also built into a #25 O-ring joint except that the joint was mounted behind the cell body such that when mounted in the TDMS chamber, the 0.110 in. dia. opening of the cell rested about 0.25 inches from the wafer surface. The cell was constructed such that all surfaces exposed to the vacuum were bathed in heating fluid during carrier volatilization. This was to allow for degassing the vacuum exposed surfaces during a pre experi-

ment carrier degas procedure, but more importantly to provide for heating of the entire exit hole of the cell.

Materials

Substrates

The substrates used in this study were provided by The Harris Semiconductor Corporation. Two types of 4 in. dia. wafers were provided: blanket tungsten on both the frontside and the backside of n-doped single crystal silicon wafers and wafers with tungsten patterned on the frontside of n-doped silicon and a blanket coat on the backside. All tungsten coats were deposited by CVD from the carbonyl. Patterned tungsten films were formed lithographically by a reactive ion plasma etch. Typical film thickness, as reported by the supplier, was of the order of 5000Å. Wafers were cleaved into desired sizes after scratching with a diamond scribe along perpendicular rational planes. Cleaning for the initial experiments consisted of scrubbing with a mild detergent followed by rinsing in flowing tap water followed by rinses in acetone and methanol before blowing dry under either nitrogen, helium, or argon gas flows.

Gold Carrier Compounds

Two gold carrier compounds were synthesized for use in these studies: trimethyl siloxane gold triphenyl phosphine and triethyl phosphine gold chloride. The compounds were

synthesized in the laboratories of Dr. Gus J. Palenik of the Department of Chemistry at the University of Florida.

Chapter IV EXPERIMENTAL METHODS AND OBSERVATIONS

The previous chapter described all apparatus, instrumentation and materials used in these studies. This chapter describes all methodology used in the examination of the selective CVD problem as well as descriptions of important observations from the experiments performed. Analytical results from the catalytic study are also presented in this chapter. Discussions of those results as well as result summaries and discussions from all other experiments are given in Chapter V.

Gold Carrier Identification

The purpose of these experiments was to identify a suitable volatile gold carrier for use in subsequent selective deposition studies. Two candidate compounds, triethyl phosphine gold chloride and triphenyl phosphine gold trimethyl siloxane were examined. An ampule containing each compound and a tungsten ribbon was prepared as described in Chapter III. The tungsten ribbon was precleaned by dipping in a 49% by weight hydrofluoric acid solution for several minutes then rinsing with deionized water followed by acetone then drying under a flow of nitrogen. The bottom of an ampule containing the respective gold carrier compound

was placed in the drilled cavity of the aluminum heater alongside the thermocouple. The well was filled with silicon based heat transfer fluid. The tungsten ribbon was then irradiated with light from the argon ion laser. The heating mantle was then turned on and the compound temperature slowly raised while observing the system's behavior (ie. melting, decomposition in the melt, gold film formation on tungsten, etc).

The first compound tested, trimethyl siloxane gold triphenyl phosphine, demonstrated unacceptable behavior for use in future experiments. Upon the commencement of heating, the compound began to decompose. No melting was observed and no gold deposit was discernable on the tungsten ribbon. At about 100°C, the compound in the well decomposed to a black tarry mass.

The second compound tested, triethyl phosphine gold chloride demonstrated quite different behavior. At about 50°C (below the melting point of about 86°C) the compound began to sublime forming a white film (the compound is a white spiny crystalline solid at room temperature) in the upper cooler regions of the sealed test ampule. No noticeable decomposition of the compound in the melt was observed. A visually thick gold film formed on the tungsten ribbon. When the tube was cleaved open, and a new ribbon was inserted and the tube then resealed in the manner described in the previous section, the identical behavior was observed. Thus the compound did not seem to be effected by cycling in and

out of vacuum. Based on these observations, triethyl phosphine gold chloride was chosen for use as the volatile gold carrier for the remainder of the studies.

Pulsed RF MOCVD Experiments

The purpose of these experiments was to determine if the skin effect from radio frequency induced eddy currents in tungsten thin films patterned on silicon substrates could be used for localized Joule heating to promote selective decomposition of the gold carrier on tungsten alone. Deposited gold films were judged visually as to the degree of selectivity on patterned wafers as well as on blanket tungsten and uncoated silicon wafers that had previously been etched of any deposited thin films. Adhesion of the films was judged by wiping the wafer after deposition with a Kimwipe paper tissue.

Initial test of the method's viability was performed by subjecting both a blanket tungsten and bare silicon wafer (prepared by dissolving the tungsten film in a potassium ferrocyanide solution)⁸⁰ to continuous RF (13.56 MHz) power and then ascertaining any heating either visually or by touch. Both of these tests were conducted at atmospheric pressure with the reactor cell body open to the air. Silicon wafers that had been stripped of any tungsten films showed no heating when exposed to an RF field of 500 watts forward power. Wafers with blanket tungsten on both sides

glowed red hot instantaneously when subjected to the same conditions. This indicated that the method was viable.

The remaining experiments were conducted under vacuum conditions with the reactor charged with carrier compound. Typically, about 100 milligrams of compound was placed in the volatilization cell. A patterned substrate wafer was then loaded on the Macor stage and placed into the reactor body such that the wafer was midway between the ends of the inductor coil, and the surface to have gold deposited on it faced the volatilization cell. The system was then rough pumped to about 1×10^{-2} torr, and then the ball valve was opened for further pumping through the bell jar diffusion pump. Once base pressure was reached (as measured by the bell jar ion gauge and typically about 1×10^{-6} torr), the RF system was started at a predetermined frequency and pulse width. The valve to the water circulator was then opened to heat the compound. At the conclusion of a run, the RF power was discontinued, the water circulator was turned off, and upon cooling of the reactor the valve between the bell jar and the CVD reactor was closed and the reactor backfilled with argon through the valved side of the volatilization cell.

Typically, gold thin films would grow at pulse widths greater than 0.1 seconds and repetition rates of 1 per second and below. Many different combinations of pulse widths and repetition rates were tried, but no selective gold thin films were observed. The success of these experi-

ments, though, was that differential growth of gold with apparent favor toward thicker growth on tungsten was observed. This observation prompted the next study to see if tungsten itself would serve as a heterogeneous catalyst for the promotion of selective gold thin film growth under constant and much more controlled temperature conditions. Those experiments are discussed in the next section.

Selectivity From Catalytic Activity Differences

The purpose of these experiments was to determine if tungsten catalyzes decomposition of the gold carrier compound at temperatures below those at which the carrier decomposes on silicon. The experimental procedure was similar to that followed during the RF tests. Tungsten patterned wafers were placed on the slanted wafer heater stage such that the patterned surface faced the exit hole from the carrier compound volatilization source. As in the RF experiments, about 100 mg of carrier compound was loaded into the volatilization cell, then the system was sealed from the atmosphere and rough pumped to about 1×10^{-3} torr. The valve separating the reactor from the diffusion pumped bell jar was then opened and the reactor pressure reduced to about 1×10^{-6} torr. The wafer temperature was set by adjusting the Variac while monitoring the temperature as indicated by the thermocouple emf reading on the multimeter. Once the proper wafer temperature was reached, the valve controlling hot water flow to the volatilization cell water

jacket was opened which marked the beginning of a deposition run. Typical deposition time was 1 hour. In a modification of the procedure, the reactor was first assembled and pumped with the rough pump alone and no carrier compound present in the volatilization cell. The wafer was heated to about 500°C while argon gas at about 1 torr pressure was flowed through the reactor for about 72 hours in order to aid in cleaning the wafer. The heater stage was then cooled and the reactor backfilled with argon. With argon flowing across the wafer, the volatilization cell was then charged with carrier compound then the reactor was sealed and pumped as described above. The experimental runs then proceeded as described above.

When a wafer was subjected to conditions of the last modification then processed at stage temperatures of 500°C and carrier temperatures of 95°C, a highly selective gold on tungsten film resulted. Figure IV.1 is a photograph of the post deposition wafer surface. It shows a high degree of selectivity as is confirmed in the scanning Auger plot of Figure IV.2. Scanning Auger spectroscopy measures relative elemental abundance from secondary electron emissions from surface species as the primary electron excitation beam is translated along a line on the substrate surface. Scanning electron microscopy (SEM) of the gold deposition showed disconnected grain growth within the deposits (Figure IV.3). The gold films proved quite pure as demonstrated by a

sputter Auger scan (Figure IV.4) of a portion of the same wafer.

Although many tests of selectivity were performed in this system, the reproducibility of deposits from run to run under apparently identical conditions was poor. At the beginning of this series of experiments, it was assumed that the substrate temperature would track the wafer stage temperature repeatably. This was evidently not the case. Non reproducibility of wafer contact on the ceramic stage was one problem source as gold would tend to deposit on the stage, and since the test wafers were not of uniform size, stage/wafer contact differences were inherent. This then allowed for differences in thermal distribution profiles from run to run. Another source of temperature variation resulted from radiant emissions from the wafer surface. Gold thin films as well as condensed carrier vapors tended to accumulate on the walls of the reactor cell. Thus the wafer surface was confronted by surfaces of varying thermal emissivity and reflectivity which, for the narrow temperature ranges subsequently found to be conducive to selectivity (to be discussed in the next section), could have profound effect on the deposition activity. Cleaning of the inner cell walls resulted in the eventual etching and further modification of wafer thermal emissions.

One other notable result of these experiments concerns gold film adhesion. As varying degrees of film selectivity

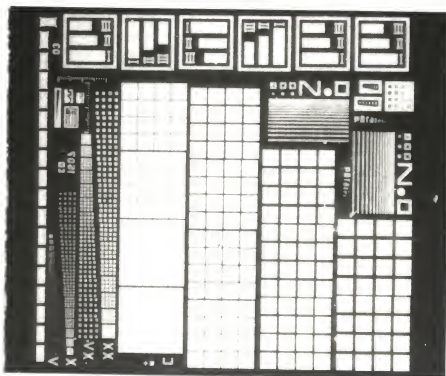


Figure IV.1. Photograph of selective gold on tungsten deposit.

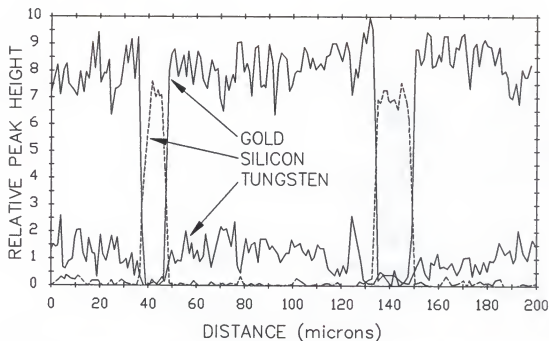


Figure IV.2. Scanning Auger spectrum across features of wafer in Figure III.1.

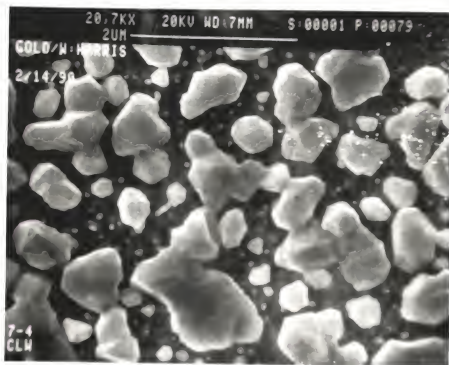


Figure IV.3. Scanning electron micrograph of selective gold deposit showing area of discontinuous growth.

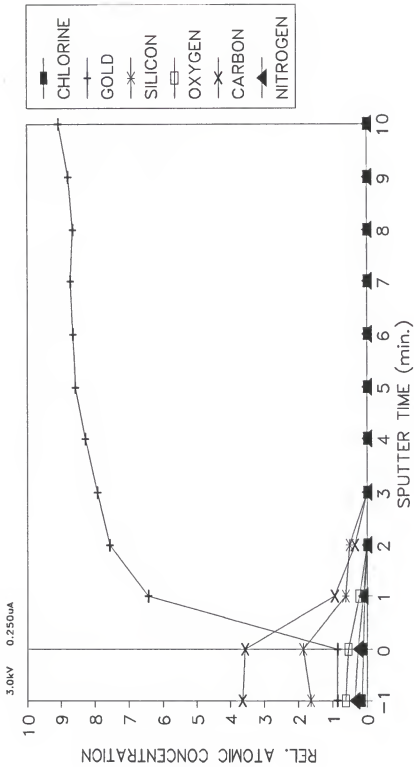


Figure IV.4. Sputter Auger profile of selective MOCVD gold film.

were noted as described above, so were varying degrees of film adhesion. Testing of film adhesion was typically performed by simply wiping the wafer surface with a tissue paper. Some non selective gold films were non adherent to both tungsten and silicon as the film over the entire surface was easily removed by even light wiping action. Some films, however, demonstrated very good adhesion to tungsten while the film on the silicon areas wiped clean. No films were observed which were adherent to silicon at any time (except in a case to be described in the next section). Figures III.5 and III.6 are scanning electron micrographs of a feature array and enlarged feature area respectively that were wiped after a non selective gold MOCVD run.

Wafer Precleaning Tests

The non reproducibility of film adherence described in the last section indicated that a vigorous, systematic wafer precleaning regime was needed. Several wafer pre cleaning treatments were tested for their effect on gold film quality and/or selectivity of deposits, but the primary motivation was to find a pretreatment that yielded reproducible and adherent films. Each precleaning test included a detergent scrub with a soft bristled brush followed by a rinse in flowing tap water. Following this, the wafer was dipped in cleaning test solution then rinsed again in flowing tap water for several minutes followed by a rinse in deionized water. Each wafer was then rinsed in spectral

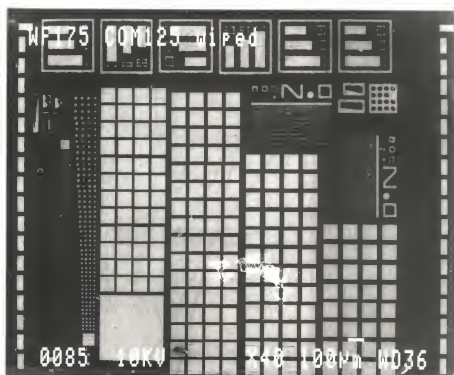


Figure IV.5. Scanning electron micrograph of wafer feature array wiped after non-selective gold MOCVD.

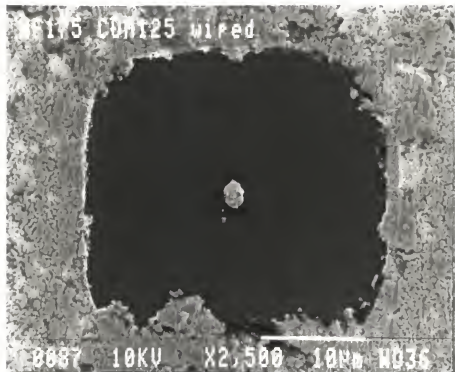


Figure IV.6. Scanning electron micrograph of wafer feature wiped after non-selective gold MOCVD.

grade acetone followed by a rinse in spectral grade methanol before drying under a flow of dry nitrogen. The wafers were then observed under an optical microscope for any deformities and those wafers showing no apparent damage were then subjected to gold MOCVD as described in the above section on catalytic deposition.

Patterned wafers were exposed to test solutions of various concentrations of aqueous hydrofluoric acid, potassium hydroxide, nitric acid, sulfuric acid, hydrochloric acid and mixtures of sulfuric acid or formic acid in aqueous hydrogen peroxide. All test solutions except for dilute HF and the formic acid/peroxide mixtures visually damaged the wafers or produced variable unacceptable deposits. The HF test solution (approximately 5% HF by weight) yielded a wafer that upon exposure to vapors of the gold carrier under similar conditions to those of the successful deposition in the catalytic studies appeared to have a reverse selective highly adherent gold film (gold on silicon to the exclusion of tungsten). Adhesion was tested by wiping with a tissue paper.

The wafer pretreatment which was adopted for use in the remainder of the deposition studies was a modified version of a method for cleaning various parts for use in high vacuum and described in the service manual for the Finigan 3200/3300 mass spectrometer system described below. The pretreatment consisted of dipping the wafer in a solution prepared by adding 4 milliliters of 30% hydrogen peroxide

and 38% formic acid each to 16 milliliters of deionized water. The solution was first heated to 80°C before the wafer was dipped for 5 seconds. Following this, the wafer was rinsed under flowing tap water for 5 minutes then rinsed with deionized water before rinses with spectral grade acetone followed by spectral grade methanol. The wafer was then dried under a flow of nitrogen. Wafers treated in this manner produced films of both repeatable quality and of acceptable adherence.

Measurement of Carrier Vapor Pressure and Tungsten Reaction Probability

The compound vapor pressure was measured using a Knudsen cell similar to the one described in Chapter III for the RF and catalytic studies, but having no gas inlet end so that the cell walls were bathed with circulating fluid uniformly in the cell. The experiments were conducted in the TDMS apparatus described in Chapter III. Full details and results are discussed in Chapter V.

Identification of Optimum Deposition Parameters

The purpose of these experiments was twofold. Firstly, since the results of the catalytic experiments described above were not readily reproducible, a system was needed to gain finer control over deposition parameters. Secondly, the need existed to identify the values of the primary parameters, which were determined to be the wafer tempera-

ture and compound vapor pressure, that resulted in selective gold thin film growth. The study consisted of three parts:

- 1) preliminary tests to determine parameter value regions for systematic study
- 2) a systematic study of selectivity in the region defined from the preliminary tests
- 3) scanning electron microscopy and energy dispersion spectroscopy of films deposited in the matrix trials for qualitative determination of optimum parameter regions.

Preliminary Optimization Tests

Qualitative results of previous experiments on selective gold deposition indicated that the useful gold carrier compound temperature is below 130°C. Above that temperature significant decomposition of the carrier occurred in the melt. Also at carrier temperatures below 90°C deposition rates were not practical. Thus at the outset of these tests it was determined that the range of compound carrier temperatures would be varied between 95°C and 125°C. The following procedure was then used to determine wafer temperature ranges.

Gold carrier was loaded into the reactor reservoir by first packing a 12 in. long piece of 1/4 in. o.d. teflon tubing with carrier then inserting this tubing through the reactor base and into the carrier reservoir. The inserted end of the tube was then gently tapped against the reservoir wall to dislodge the compound before removing the tube. One

compound loading was used in all of the preliminary tests. After cleaning as described in the previous section, a wafer was then loaded onto the wafer heater assembly and the thermocouple carefully placed on the wafer surface. The reactor sphere was then placed over the heater assembly and secured to the base plate. A new copper gasket was used for each trial. The reactor was pumped to about 0.1 torr then liquid nitrogen was poured into the trap. At this point the wafer was heated to about 120°C then the oven was heated to about 130°C. The wafer temperature was then raised in 5 degree increments every 1/2 hour until the onset of deposition was observed. This procedure was followed for three oven temperatures: 95°C, 110°C, and 125°C.

Systematic Study of Selective Gold MOCVD

Preliminary experiments indicated that the onset of gold deposition on tungsten patterns occurred at about 155°C with deposition on both tungsten and silicon occurring above 175°C. Thus a 3 level 2 factor type experimental program was performed to determine an optimum deposition point in the experimental plane. The experimental procedure was the same as described above in the preliminary runs except that the wafer temperature was preset. All deposition times were 1 hour from the time the oven reached the set temperature.

The reactor was cleaned and a new charge of gold carrier was used in each trial. The cleaning procedure consisted of pouring methylene chloride into the reactor to dissolve the compound then aspirating all fluid from the chamber.

This was followed with rinsing/aspiration cycles of acetone then methanol. A teflon tube was then inserted into the reactor carrier reservoir and nitrogen gas was flowed through the reactor for about 15 minutes to dry the inside. After high oven temperature runs (125°C), a thin gold film formed on the inside of the reactor which was removed with an aqua regia solution after rinsing with methylene chloride. When this was necessary, the reactor was rinsed with copious amounts of tap water before the acetone/methanol rinses. Table III.1 is a complete listing of all trials in the matrix study.

Over the course of the matrix runs, problems developed with the thermocouple placed on the substrate surface. The iron/constantan couple itself exhibited selective gold film growth as gold was seen to deposit on the exposed iron wire. It is possible that solid diffusion of gold into the couple weld region or corrosion from the reaction byproducts, especially chlorine, could have had detrimental effect on the wafer temperature measurement. The digital output of the Watlow temperature controller exhibited quite erratic behavior after a thermocouple had been in use for more than two runs. This necessitated the rebuilding of the couple several times during the course of the runs. All efforts were made to weld the wire pairs in the same manner from rebuild to rebuild, but due to the delicacy of the wire (0.001 in. dia.) small differences could have large effects on reproducibility of films especially in consideration of the

noticeable temperature sensitivity of the process. Also, it should be noted that the film features on the patterned wafers would tend to cause temperature gradients over the surface of the wafer and due to the very small size of the features, repeatable placement of the thermocouple and reliable knowledge of the relative wafer temperature from run to run was not attainable. These problems will be addressed further in Chapter V.

Table III.1 Listing of selective gold MOCVD matrix experiments.

Trial Number	Substrate Temperature	Compound Temperature	Comments
1	155	110	a
2	155	95	b,e
3	165	125	b,d
4	175	110	a
5	155	125	c
6	175	125	b,d
7	175	95	b
8	165	110	b,d
9	165	95	c
10	165	110	a,e
11	155	95	a,d
12	155	110	b,e
13	155	125	b,e
14	165	110	b,d
15	165	95	b,e
16	165	125	a
17	175	95	b,e
18	175	110	a,d
19	175	110	a,e
20	175	125	a,e
21	165	110	a,d
22	165	125	a,e

- a) blanket, non selective gold coat
- b) selective gold coat
- c) no apparent coat
- d) thermocouple malfunction
- e) submitted for SEM and EDS analysis

Analysis of Gold Films From the Matrix Study by Scanning Electron Microscopy and Energy Dispersion Microscopy

The scanning electron microscopy and energy dispersion spectroscopy analyses were carried out in order to determine grain size and density, grain structure, and growth characteristics and to provide a semiquantitative determination of selectivity from sample to sample by comparing relative gold to substrate peak heights. Analysis was performed by Dr. Charles Simon at the McDonald Center for the Space Sciences at Washington University in St. Louis Missouri on a JOEL SEM equipped with an energy dispersion spectroscopy (EDS) system. Scanning electron micrographs of an entire wafer feature array, a line feature and a dot feature were produced for each of the nine wafers of the matrix study as well as one blank. In addition, interesting deposition phenomena on specific wafers were also scanned. The EDS spectra were generated by focusing at a fixed magnification (600X) on a surface area of silicon and an adjacent area of tungsten then counting for a set period (2 minutes). Thus two spectra were generated for each of the nine wafers subjected to gold MOCVD as well as two for the blank wafer. A summary presentation discussion of these results is given in Chapter V.

Thermal Desorption Mass Spectroscopy

Thermal desorption mass spectroscopy (TDMS) of the gold carrier interaction with blanket surfaces of tungsten and silicon was performed in order to derive relative

information relating to the carrier decomposition chemistry on both types of surfaces. This section presents the experimental method employed. Presentation and discussion of results is given in Chapter V.

The description of the TDMS system construction and instrumentation was presented in the previous chapter. Two experimental runs were performed with that system: one run of the carrier interaction with a wafer which had a blanket thin tungsten film on deposited on top of the silicon substrate and another run of the same carrier interaction with a surface where the tungsten film was stripped off exposing the silicon underneath.

Before a wafer was loaded into the TDMS chamber, a gold carrier compound sublimation step and vacuum system bake out was performed. About 1.5 grams of the triethyl phosphine gold chloride carrier was loaded into the volatilization cell then attached to the TDMS chamber. The chamber was then pumped by first starting the turbo molecular pump then starting the backing pump. This was done in order to minimize oil backstreaming from the backing pump into the TDMS reaction system. After a base pressure had been established (typically of the order of 1×10^{-7} torr before bakeout) a solution of ethylene glycol in water heated to 110°C was circulated through the jacket of the volatilization cell. This melted the compound and allowed for outgassing. After several minutes and when no more outgassing in the melt

could be observed (the pressure gauge and mass spectrometer signals showed no further response), cold water was immediately introduced into the cell jacket solidifying the carrier compound. Cold water was continued circulating while the heating jackets on the TDMS chamber, the mass spectrometer chamber, and the turbo molecular pump body were turned on to bake the chamber. Typical bake outs of 24 hours removed all signals generated by the carrier compound in the mass spectrometer and allowed for the attainment of base pressures of 1×10^{-9} torr when the liquid nitrogen wafer isolation trap was filled. No mass spectrometer signal from the gold carrier could be seen from its presence in the volatilization cell at room temperature.

After the bake out period, the vacuum system was shut down by turning the turbo molecular pump motor off then leaking nitrogen gas into the system through a valve located at the exit port of the turbo pump. This served the dual purpose of slowing the pump rotor through momentum transfer with the pump rotors and minimized mechanical pump oil back streaming. When the turbo pump rotor had slowed sufficiently, an isolation valve located between the turbo and mechanical pump was closed and nitrogen gas was introduced into the TDMS system until a slight positive pressure relative to atmosphere existed. At this point the substrate support flange was dismantled from the chamber. A wafer cleaned in the manner described earlier in this chapter was mounted making sure the thermocouple was properly placed on the

surface in the reaction zone. The flange was then remounted to the chamber and the pumps started as described above to minimize oil backstreaming. After base pressure was established, the heating jackets were again turned on and the chamber baked overnight.

At the beginning of an experimental run, the heating mantles were turned off and the system was allowed to cool to room temperature. The liquid nitrogen wafer isolation trap was then filled. When the base pressure of the system reached 5×10^{-9} torr, the argon ion laser was directed at full power onto the back of the wafer to outgas and otherwise clean it. The wafer surface was typically brought to about 300°C for several minutes then allowed to cool to room temperature.

The computer control system could produce and store a full 400 atomic mass unit scan, averaged over 5 scans, approximately every 2.5 seconds. Typically during an experimental run, 500 such scans were generated. In order to minimize computer hard disc access time, the files to receive the data were first created and stored on the hard disc. Also during the course of a run, all data were stored in binary arrays in random access memory during each scan and averaging step. This allowed for maximum efficiency in writing the data to the hard disc in minimum amount of time.

Once the wafer had cooled and the computer control system was set, the computer was started to allow the capture of about 10 scans in order to establish the background

signals for latter reference. The same ethylene glycol heating fluid described above at a temperature of 110°C was introduced into the volatilization cell and upon settling of the pressure and mass spectrometer signals (typically about 10 more scans) the laser beam was directed at half power (2.5 watts) onto the wafer backside. After 200 total scans had been performed, the laser was turned to full power for another 100 scans then the beam was blocked allowing the wafer to cool rapidly. The final 200 scans were captured during this cooling period.

At the conclusion of the two runs, representative mass spectra taken well into the first wafer heating cycle were generated and peaks associated with the experimental procedure were identified. Software was written which could integrate the peaks for each scan and for graphical presentation of these mass integration values versus time.

CHAPTER V RESULTS AND DISCUSSIONS

In this chapter interpretive discussions and results of all experiments are given. Each experimental procedure and result(s) is treated separately, as in the previous chapter. Some conclusions indigenous to the section under discussion are presented. Conclusions relating each section to the overall purpose of the entire study are saved for Chapter VI.

Gold Carrier Identification

The two gold carriers tested, trimethyl siloxane gold triphenyl phosphine and triethyl phosphine gold chloride, demonstrated different behaviors under the test conditions. The behavior of the former was somewhat predictable since gold(I) complexes with oxygen donors have generally low thermal stability, decomposing to gold metal.⁸¹ Therein lies the primary reason for examining this compound, as a facile surface decomposition was desired. An analogous compound, trimethyl siloxane gold trimethyl phosphine, is reported to have relative high thermal stability and can be sublimed under vacuum without decomposition.⁸¹ In terms of the ordering of the relative stabilization effects of the phosphine ligand series, triphenyl phosphine forms a less

stable complex than the trimethyl analogue due to steric effects.⁸¹ It seems then, for future work, the trimethyl derivative might hold promise as a volatile carrier.

The relative standard redox potentials of gold in forming gold(I) complexes with oxygen and chlorine gives an indication of respective stabilities. Gold is much more easily oxidized in the presence of chlorine (+1.15V) than in the presence of water (+1.7V). Thus gold forms a stable chloride existing as a two coordinate polymeric crystal in the solid state. By passing a trialkyl phosphine over the heated solid, the trialkyl phosphine gold chloride monomer can be captured downstream.

This stability in the vapor phase was demonstrated in the test with triethyl phosphine gold chloride as repeated evaporations were possible with little or no apparent decomposition except on the heated tungsten ribbon as desired. In the case of the trimethyl siloxane species, bond breaking enthalpies are probably lower than evaporation or sublimation enthalpies; if so it would tend to decompose with no apparent volatilization as was observed.

RF MOCVD

The primary result of the RF experiment was the observation of somewhat preferential growth of gold films on tungsten wafer features relative to growth observed on tungsten. This observation prompted the experiments on catalytic activity which is the primary topic of discussion

in the remainder of this chapter. Other observations relating to the heating effects of the RF fields on the thin tungsten films are of interest in terms of their potential for application to MOCVD.

The initial experiments described testing of the method's viability by placing blanket tungsten coated wafers and bare silicon wafers in the RF field and observing any heating by simple touch or by sight. It was apparent, from the heating of the tungsten clad wafer, that conducting electrons in the thin tungsten films were strongly coupling with the RF field. When the wafer was slightly tilted in the magnetic field, though, no heating was observed which implies a cosecant fuctional heating distribution dependnece. In RF heating, the depth of substantial magnetic field penetration is inversely proportional to the excitation frequency. The "skin effect" or penetration depth is the depth at which the magnetic field strength falls to $1/e$ (0.368) of its value at the surface and is given by⁶⁴

$$\delta = \sqrt{\frac{\rho}{\mu f \pi}} \quad \text{V.1}$$

where ρ is the resistivity, μ is the magnetic permeability, and f is the excitation frequency in cycles per second and δ is the skin depth. In tungsten at frequency of 13.56 MHz the skin depth is about 3000Å. The magnetic field penetration depth is of the same order as the tungsten films are

thick and, thus, an anomalous effect might be expected. Indeed the anomalous skin effect has been used to measure and study the penetration depth on inclination substrate inclination angle⁸⁵ as well as to study conductivity in "odd" geometry metals and alloys.⁸⁶

As the application of RF field in this work involved a pulsing to eliminate heat build up. One can envision, with respect to the above discussion, an experimental regime where instead of pulsing the RF, the sample could be rotated in the magnetic field and thus be "pulsed" as the film plane lines up with the magnetic field vectors. This could be of advantage in situations where the deposition rate was diffusion limited as the rotation would tend to "stir" the ambient gas.

As was discussed in Chapter IV, tungsten coated wafers tended to glow red hot almost instantaneously when exposed to the RF fields. In consideration of the small relative surface area of the tungsten patterns on the silicon surface and the fact that silicon alone showed no such action, it seems possible that the semiconductor absorbed heat from the film thereby reaching sufficient temperature to promote electrons into conducting bands, thus allowing it to be further heated by the inductive effect. It seems unlikely that the rapid glow could be caused by coupling with the tungsten alone because in that case the silicon substrate behave initially as a substantial heat sink.

One final comment dealing with possible improvements on the technique involves the construction of the RF coil. The coil in this work was hand wound and thus probably lacked sufficient geometric isotropy to produce an RF field of high homogeneity as would probably be necessary for this type of application. Such concerns have been addressed in terms of similar coils constructed for pulsed NMR systems where the free standing coils have been replaced by boron nitride external supports for a machine wound coil.⁸⁷ Another problem that needs to be addressed for the advancement of this technique is coil geometry in terms of winding pitch spacing and variance. As thin film deposition, and selective deposition in particular, are carried out at smaller and smaller geometries, the RF heating technique could be used to great advantage in many situations where simple chemical differentiation of surface structures is not possible.

Catalytic Differentiation of Surface features for Selective MOCVD

These experiments were performed to show that selective MOCVD was indeed possible on a tungsten patterned silicon surface which was held at a constant temperature over the entire surface. Due to lack of precise knowledge of the true surface temperature and due to lack of close control over the deposition in general as evidenced by the non repeatability of depositions in this study, discussion of physical and chemical aspects of the process are deterred to

the last two sections of this chapter which deal with the better characterized matrix and thermal desorption studies. Two results that will be discussed here deal with film purity and film adhesion.

As can be seen from the sputter auger profile, after several minutes of sputter time to remove contaminants that had accumulated after the experimental run, all signals, except for gold, fell below the auger detection limits. This indicated a well defined and clean decomposition mechanism on the tungsten surface. This fact is a key to the decomposition mechanism presented in the final section of this chapter. Of greater importance, in terms of a commercial process, it implies that the films are of high potential conductivity when they are continuous. The SEM of the growth structure demonstrate the problems encountered with this growth and are addressed in the next two section dealing with surface cleaning and the matrix studies.

The differential adhesion observed by the wiping of the non selective films is a possible key in understanding the selective deposition process. It implies that chemisorption is occurring on tungsten while weaker physisorption forces are dominant on silicon. This topic will be considered further in following sections of this chapter.

Wafer Precleaning Study

As stated in the previous chapter, the wafer precleaning studies were performed in order to achieve film growth

of both reproducible quality and acceptable adhesion. Since the wafers were received in shipping containers from a clean room environment, as received surface condition should have been optimal. Still, handling had to be done in order to cleave and otherwise prepare the substrates for use in deposition studies. Thus the primary contaminants probably were organics originating from air borne sources and unavoidable touching of the wafer surfaces even though plastic gloves were used in most handling operations. Thus, gross contamination was removed with the detergent scrubbing and more tenacious coverage was attacked by the hot oxidizing peroxide solution.

Vapor Pressure and Tungsten Reaction Probability

The kinetics of chemical vapor deposition reactions depend on many factors. Some, such as the mechanistic steps acting at the atomic and molecular level, are determined by the specific chemistry of the process. Others depend more on the experimental conditions under which the process is carried out. Information which is useful in planning or interpreting CVD experiments includes knowledge of: the rate of arrival of carrier molecules at the substrate; sticking coefficients; rates of desorption of carrier molecules and reaction by products, surface mobilities of absorbed species and the influence of surface irregularities and foreign atoms or molecules. Although it may at times be desirable to grow films by CVD in simple vapor filled

reactors, it is preferable for investigating the CVD process itself to house the substrate in a continuously pumped vacuum chamber and expose it to a reasonably characterized effusive stream of carrier molecules. This arrangement avoids the complications which otherwise result from diffusion effects which limit the flow of species to and from the surface.

To gain insight to the behavior of carrier gas on the substrate, it is desirable to know the flux of molecules onto the surface and the corresponding rate of film growth. The reactant flux may be deduced from knowledge of the vapor pressure in the effusion source and details of the geometric arrangement of source and substrate. These concepts are illustrated below for the CVD of triethylphosphine gold chloride.

The vapor pressure of liquid triethylphosphine gold chloride was reported to be 0.03 torr at 483K.⁴⁵ To obtain a vapor pressure value at another temperature, a Knudsen cell evaporation experiment was carried out employing the cell described in the section on TDMS apparatus in Chapter III. The time rate of loss of mass by effusion into a vacuum through a circular channel of 0.28cm diameter and length/diameter ratio = 2 was found to be 6.23 mg hr⁻¹ at 368K by observations over periods of several hours. These data support a calculation of the source gas vapor pressure using the theory of free molecular flow.^{86,87} The theoretical relationship may be written

$$P = \frac{-(dW/dt)}{A_s f_c} \sqrt{\frac{2\pi RT}{\bar{M}}} \quad \text{V.2}$$

where P is the vapor pressure, $-dW/dt$ is the mass loss rate of the effusion cell, A_s is the cross sectional area of the source channel, $\bar{M}$ is the molar mass of the evaporant and f_c is the Clausing factor, which corrects for the finite length of the source channel. For the present cell $f_c = 0.51$, and introducing this value along with the other parameters stated above gives $P = 9.7 \times 10^{-4}$ torr at 368K. It is known that for the most accurate vapor pressure measurements using the effusive flow technique it is necessary to correct for nonuniformities of vapor density inside the cell.^{91,92,93,94} These refinements were not needed for the present work which requires only reasonable estimates of the vapor pressure and corresponding parameters.

The vapor pressure at other temperatures and the average heat of vaporization of the gold compound may now be inferred from the Clausius-Clapyeron Equation

$$\ln(P_2/P_1) = \frac{\Delta \tilde{H}_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) . \quad \text{V.3}$$

Using the vapor pressure data

T	P
368K	9.7×10^{-4} torr
483K	3.0×10^{-2} torr

one finds $\Delta H_v = 44 \text{ kJ mole}^{-1}$. Substitution of this result into Equation 2 above yields

$$P_T = (9.7 \times 10^{-4} \text{ torr}) e^{5292K \left(\frac{1}{368K} - \frac{1}{T} \right)} \quad \text{V.4}$$

In a typical CVD experiment using a tungsten substrate exposed to an effusive steam of carrier vapors the film growth rate was found to be about $1000 \text{ \AA hr}^{-1}$ when the substrate was heated to 388K while exposed to the Knudsen cell described above at a distance of 2.5cm from the source and tilted so that the normal to the substrate surface makes an angle of 30° with respect to the effusive beam axis. The cell temperature was 368K. For this arrangement the flux of carrier molecules Γ_n onto the substrate in the vicinity of the beam axis is given by⁸¹

$$\Gamma_n = \frac{A_s P_s \cos \theta}{2\pi L^2 kT} \sqrt{\frac{9\pi kT}{8m}} \quad \text{V.5}$$

where A_s is the cross sectional area of the source channel, P_s is the source pressure, L is the distance from the source to the substrate, k is Boltzmann's constant, m is the molecular mass and θ is the angle of incidence of the beam on the substrate. This result permits the calculation of the maximum film growth rate under these conditions assuming that each carrier molecule striking the substrate decomposes, leaving its gold atom in the film, which itself has the density of bulk gold. Consider an element of surface area A_f on the substrate in the beam axis. If l is

the film thickness there, then the density is $\rho =$
mass/volume = $W/A_F l$, and the rate of film growth is

$$\left(\frac{dl}{dt}\right)_{\max} = \frac{dw/dt}{A_F \rho} = \frac{\Gamma_m A_F}{A_F \rho} = \frac{\Gamma_m}{\rho} = \frac{m \Gamma_n}{\rho} \quad \text{V.6}$$

Taking $\rho = 18.88 \text{ g cm}^{-3}$ and using the other values stated above gives

$$\left(\frac{dl}{dt}\right)_{\max} = 3.7 \times 10^3 \text{ \AA hr}^{-1} \quad \text{V.7}$$

Comparison of this result with the observed film growth rate ($1 \times 10^3 \text{ \AA hr}^{-1}$) indicates that the CVD efficiency is approximately 27% under these operating conditions, or that about one in four carrier molecules decomposes on impact with the surface. The others must re-evaporate before decomposition occurs. These results, while only approximate, still aid in understanding the effects of operating conditions on the film generation. Faster growth rates could perhaps be achieved by exposing the substrate to a broader source or to multiple sources, but ultimately diffusion effects would most likely become limiting.

Selective Film Deposition Parameters

The original purpose of these experiments was to employ a statistical design technique in order to identify optimum values of deposition parameters. However, such programmed analysis is dependent on the non variance of experimental conditions except for those purposely altered.⁹⁵ Problems with the thermocouple have already been discussed. The most

severe problem in terms of repeatable conditions arose from the slow temperature rise time of the oven. All depositions were timed at an hour from the moment the oven reached the carrier compound set temperature. The temperature rise times, though were of the order of 20 minutes at 125°C and about 10 for 95°C. Although unavoidable, it was assumed that this source of error along with the wafer temperature measurement uncertainty would result in misleading conclusions derived from a full statistical workup. Thus the following analysis is based on qualitative observations of SEM results and semiquantitative treatment of EDS findings.

Trends relating the deposition parameters to selectivity, gold grain size and film coalescence behavior are evident from the SEM results. Figures V.1 and V.2 show SEM images of features from wafers processed at low compound temperature and low and high surface temperature respectively. The surface temperature variation in this region appears to favor selectivity at higher surface temperature as well as smaller grain sizes. The average grain size trend is in direct contradiction to gold films grown by sputtering or evaporation where increased surface temperatures tend to yield larger grains.⁹⁶ Gold films grown in those manners, unlike those grown by CVD, do not result from chemical reactions. The present observations would seem to indicate that at low vapor flux rates on tungsten higher surface temperatures result in increased decomposition probability. As can be seen in Figure V.3 of

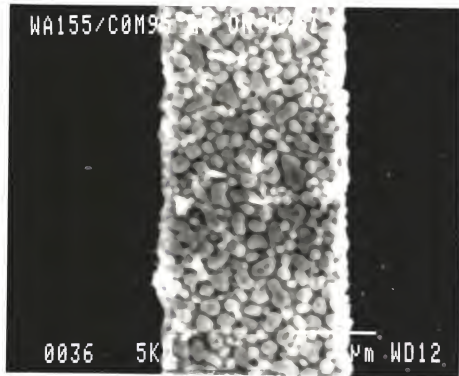


Figure V.1. Scanning electron micrograph of substrate feature from wafer processed at a surface temperature of 155°C and with the carrier temperature set at 95°C.

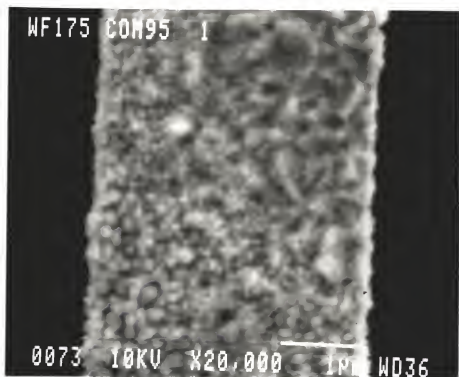


Figure V.2. Scanning electron micrograph of substrate feature from wafer processed at a surface temperature of 175°C and with the carrier temperature set at 95°C.

a pre gold deposition tungsten feature, the surface is multicrystalline and highly faceted implying a distribution of sites of various surface energies.⁹⁷ Thus, at low surface temperatures decomposition occurs only at sites of the strongest surface binding energy while at higher surface temperatures sufficient thermal energy is available at weaker binding sites to promote decomposition and an increased grain density. Selectivity at the higher wafer temperature appears to be a function of the nucleation probability as discussed in Chapter II. This can be seen

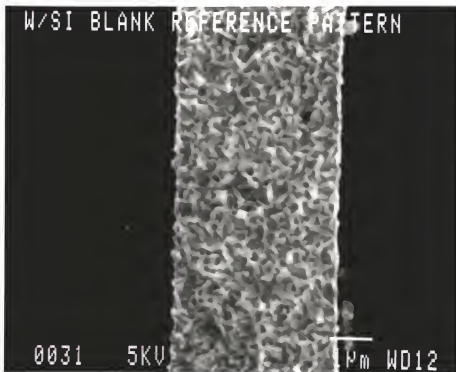


Figure V.3. Scanning electron micrograph of tungsten feature from uncoated wafer.

with regard to Figure V.4 of a film grown at high wafer temperature and high carrier temperature. Thus the increased surface flux resulted in surface aggregate free energy fluctuations from the increased in supersaturation. These trends were evident to a somewhat lesser degree in wafers at the lower temperatures.

Gold films began to show coalescence of grains into continuous films at the highest wafer temperature and highest carrier fluxes, yet selectivity was poor. This is evident in Figure V.5 of a nonselective film grown at high surface temperature and medium carrier temperature. Of particular note here, though, is the area of selectivity surrounding the tungsten dot in the center of the photograph. This behavior is also seen in Figure V.4. Upon close examination of that image a difference in the silicon surface can be seen as a shadowing especially in the region of the lower right dot. This indicates a difference in surface treatment during etching that in some cases allows for selectivity at temperatures where the gold films are coalescing on tungsten. It is unknown what this modification is, but its determination and subsequent application could be important for the formation of highly conductive selective gold films.

Figures V.6 and V.7 are EDS scans from wafers in Figures V.1 and V.4 respectively. Grain coalescence trends are evident in the upper spectra of each figure from scans gathered on tungsten features. Tungsten signals are evident

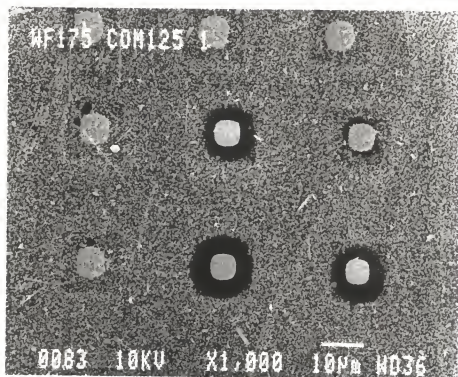


Figure V.4. Scanning electron micrograph of substrate feature from wafer processed at a surface temperature of 175°C and with the carrier temperature set at 125°C.

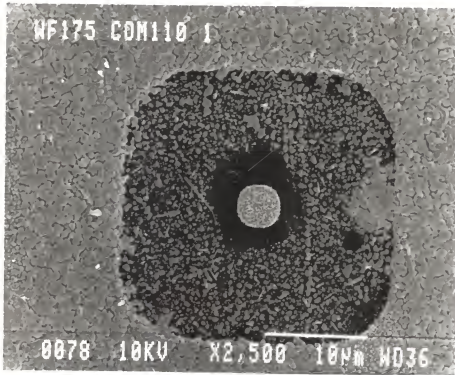


Figure V.5. Scanning electron micrograph of substrate feature from wafer processed at a surface temperature of 175°C and with the carrier temperature set at 110°C.

in Figure V.6 resulting from the barrier exposure between grains. No signals from tungsten can be seen in Figure V.7. indicating continuity. Selectivity trends are demonstrated in the lower spectra of each figure taken from silicon areas. In Figure V.6, no gold signal can be seen while the silicon scan of Figure V.7 an intense gold signal is apparent. These results are indicative of trends throughout the entire series and are summarized in Figures V.8 and V.9 of carrier isotherm plots of relative gold $M\alpha$ signal intensities versus surface temperature. All signals were corrected for background. The signals gathered from the silicon areas in Figure V.8 support the critical aggregate size model discussed for the SEM findings above. Signals from tungsten areas seem to indicate a mass transport limited reaction at lower compound flux up to a maximum surface rate at higher fluxes.

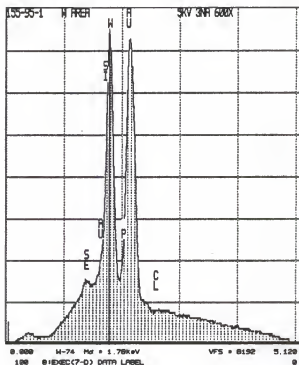
Thermal Desorption Mass Spectroscopy

Figure V.10 is a mass spectrum captured at the beginning of a typical TDMS run and Figure V.11 shows one well into the substrate heating cycle. The former was captured before the carrier or substrate heating was started thus showing the system background signals. Comparison of spectra captured for runs on silicon and runs on tungsten showed identical patterns indicating that the surface mechanistic processes were the same. Figure V.12 is a mass spectrum of triethyl phosphine gold chloride analyzed in the

Figure V.6. Energy dispersion spectra of (top) tungsten area and (bottom) silicon area of wafer processed at 155°C surface temperature and with the carrier temperature set at 95°C.

TH-5 00
Cursor-1 1.708keV = 7654

FRI 03-AUG-98 03:02



TH-5 00
Cursor-1 1.738keV = 25193

FRI 03-AUG-98 03:08

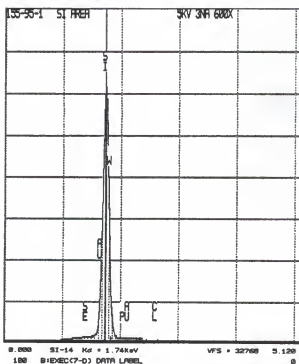
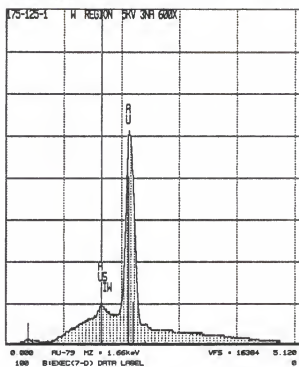


Figure V.6. Energy dispersion spectra of (top) tungsten area and (bottom) silicon area of wafer processes at 175°C surface temperature and with the carrier temperature set at 125°C.

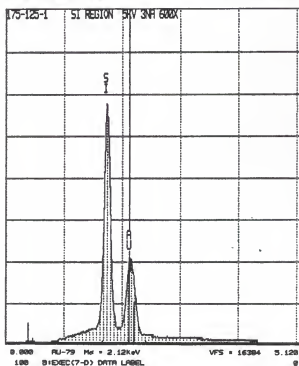
TN-5 00
Cursor:1 1.638keV + 2878

FRI 03-AUG-90 00:131



TN-5 00
Cursor:1 2.128keV + 4843

FRI 03-AUG-90 00:120



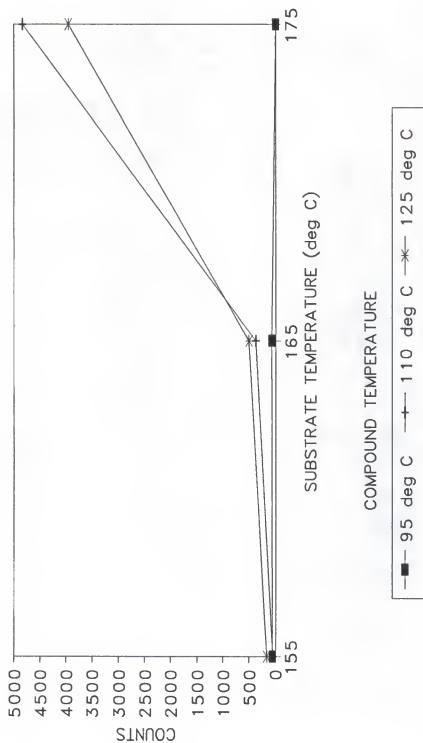


Figure V.8. Carrier temperature isotherms of gold EDS signal intensity versus substrate temperature on silicon areas.

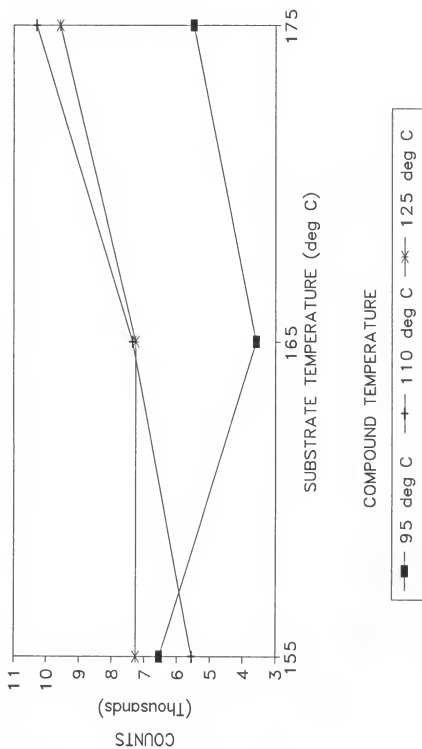


Figure V.9. Carrier temperature isotherms of gold EDS signal intensity versus substrate temperature on tungsten.

mass spectroscopy support laboratory in the UF Department of Chemistry. From this and with its included species identification, all masses in the tungsten and silicon runs were assigned. These assignments are given in Table V.1. Twenty three species were identified with some of these being attributed to vacuum system contamination.

Table V.1. Assignment of mass spectra peaks

Mass to Charge Ratio	Species Identification
35	$^{35}\text{Cl}^+$
37	$^{37}\text{Cl}^+$
40	$?\text{NO}^+$
44	CO^+
57	$?\text{C}_2\text{H}_2\text{P}^+$
62	$(\text{C}_2\text{H}_5)_2\text{P}^+$
90	$(\text{C}_2\text{H}_5)_2\text{P}^+$
103	$\text{CH}_2(\text{C}_2\text{H}_5)_2\text{P}^+$
106	Contaminant ¹
118	$(\text{C}_2\text{H}_5)_3\text{P}^+$
149	Contaminant ²
153	$(\text{C}_2\text{H}_5)_3\text{P}^{35}\text{Cl}^+$
155	$(\text{C}_2\text{H}_5)_3\text{P}^{37}\text{Cl}^+$
166	Contaminant ²
186	Re filament
197	Au^+
228	PAu^+
241	CHPAu^+
256	$\text{C}_2\text{H}_4\text{PAu}^+$
279	Contaminant ²
286	$(\text{C}_2\text{H}_5)_2\text{PAu}^+$
315	$(\text{C}_2\text{H}_5)_3\text{PAu}^+$
350	$(\text{C}_2\text{H}_5)_3\text{PAu}^{35}\text{Cl}^+$

1 Unknown contaminant.

2 Contamination from these three peaks in the same relative abundance has been seen often. They possibly derive from vacuum grease or O-ring materials.

The primary problem here is to separate the gas phase chemical processes in the mass spectrometer from the surface

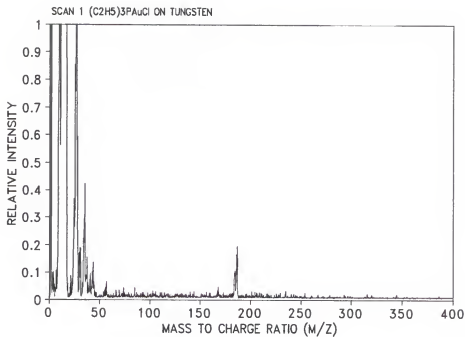


Figure V.10. Background mass spectrum before starting substrate or carrier heaters in TDMS run.

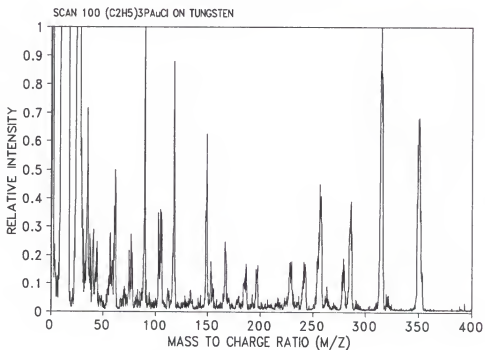


Figure V.11. Mass spectrum captured during a typical TDMS run.

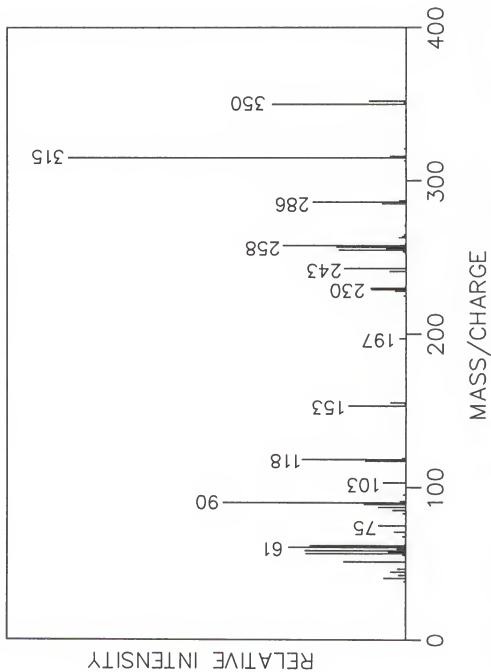


Figure V.12. Solids probe mass spectrum of triethyl phosphine gold chloride.

processes. The integration cross sections from all species were compared and from the rule that all species having similarly shaped curves derive from the same gas phase process⁹⁸ all peaks containing gold were attributed to the parent triethyl phosphine gold chloride which had escaped the surface without decomposing. In addition, peaks at $M/Z = 35$ and 37 from chlorine were identified. The intensities of each of these two peak groups were summed and their plots versus run time are given in Figures V.13 and V.14 for silicon and Figures V.15 and V.16 for tungsten. The surface heating profile is included on each plot. As can be seen, the heating profile on silicon shows a much faster rise than the profile on tungsten scans. This is due to the insulating effect of the thin tungsten film on both sides of the tungsten TDMS runs and only the back side of the silicon TDMS trial. From the intensity of the peak at mass to charge ratio 315 ($(C_2H_5)_3PAu^+$) in Figures V.11 and V.12, it can be implied that the elimination of chlorine is the most favored bond breakage in the initiation of decomposition. To be sure, since the gold is also bonded to phosphorus it can also eliminate the triethyl phosphine group, but there is no indication in any of the mass spectra of a species at $M/Z = 232$ which would correspond to $AuCl$. It should also be pointed out that the chlorine peak is relatively small in spectra evolved from gas phase triethyl phosphine gold chloride. Notice should also be made of the relative response of the parent compound and chlorine signal

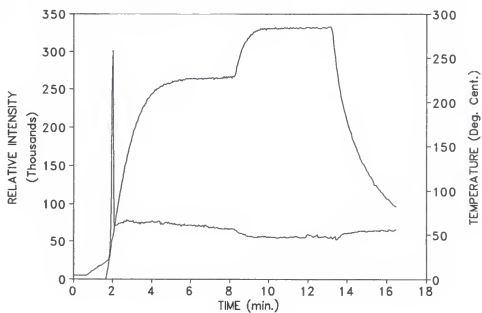


Figure V.13. Sum of gold containing peak integration cross section from TDMS run on silicon.

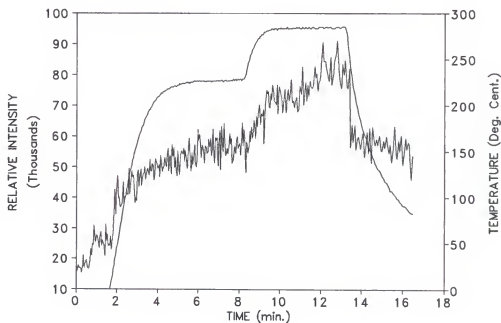


Figure V.14. Sum of chlorine isotope peaks from TDMS run on silicon.

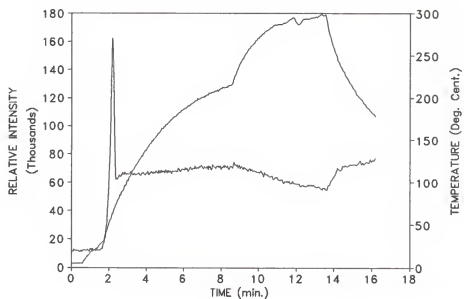


Figure V.15. Sum of gold containing integration cross sections from TDMS run on tungsten.

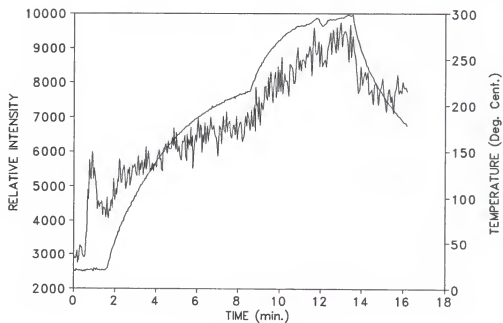


Figure V.16. Sum of chlorine isotope cross sections from TDMS run on tungsten.

sums to the heating profile. When the laser power was increased at the midpoint of a run, triethyl phosphine gold intensities decreased while a corresponding increase in chlorine signal is evident. The opposite behavior can be seen at the point where laser power was discontinued to the substrate. Comparison of Figure V.13 with V.14 and V.15 with V.16 reveals the absence of the large spike at the beginning of the surface heating cycle in the chlorine cross section. This spike in the parent compound cross section results from the flash desorption of condensed carrier in the early stages of the experimental runs. The absence of a similar flash peak along with the surface heating profile response of the cross section for chlorine implies that the latter is produced primarily on the surface. In the gas phase spectra, the only apparent chlorine containing peaks are at $M/Z = 153$ and $M/Z = 155$ which corresponds to the two chlorine isotopes of $(C_2H_5)_3PCl$. The large spikes do appear in the $M/Z = 153$ and $M/Z = 155$ cross section indicating that these are formed in the gas phase. This result is intriguing in that it implies either a unimolecular elimination of the gold atom or more probably a gas phase collision formation mechanism. Detailed treatment of this reaction, however, is beyond the scope of this work.

The primary concern here is to examine the decomposition chemistry of the gold carrier on a silicon and a tungsten surface and then relate differences in the two to the selectivity observed in earlier experiments. It was

implied from the EDS and sputter auger analysis that the decomposition is very clean in the sense that no chlorine or phosphorus contamination was seen. From this a simple decomposition mechanism is assumed. In deriving that mechanism the following assumptions are made with regard to the discussions so far:

1. The initial step of film growth on either tungsten or silicon involves the reductive elimination of a chlorine atom.
2. A steady state process for the reductive elimination is established on the surface, and the surface concentrations of reactant and product species are directly proportional to the corresponding mass spectrometer peak intensities.

Assumption 1 seems reasonable in view of the large peak in all spectra at $M/Z = 315$ and the fact that gold films do indeed form, so a reduction step must occur. It can be seen that the atomic chlorine cross sections rise steadily with the heating profiles and show definite response to sudden heating changes. Since the chlorine cross section lacks the flash desorption spike mentioned above, much of it must be produced on the surface. The surface chlorine produced apparently has either little surface mobility or is quickly desorbed since no signals for Cl_2 are observed in the mass spectra. However, triethyl phosphine chloride signals rise steadily with temperature and show rapid response to substrate heating changes implying a mobility of either

triethyl phosphine or the triethyl phosphine gold species. In the latter case, recombination with chlorine could result with subsequent reevaporation or a reelimination which would imply an equilibrium condition. Thus, the initial reaction can be written as



where the surface equilibrium constant, K, is then given by

$$K = \frac{[(C_2H_5)_3PAu][Cl]}{[(C_2H_5)_3PAuCl]} \quad V.9$$

The bracketed terms denote surface concentrations.

From the defining relation for the Gibb's free energy

$$G = H - TS \quad V.10$$

the fundamental relation

$$dG = -SdT + VdP \quad V.11$$

can be derived for reversible changes in temperature and pressure. For a constant temperature process, then, we have

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad V.12$$

Assuming ideal gas behavior, $V = RT/P$, V.12 becomes

$$dG = \frac{RT}{P} dP = RTd(\ln P) \quad V.13$$

Integration of this result for a gas in a standard reference state at some unit pressure yields

$$G = G^0 + RT \ln P \quad V.14$$

Thus for the free energy change in the reaction given in V.8 we have

$$\Delta G = (G_{(C_2H_5)_3PAu}^0 + G_{Cl}^0) - G_{(C_2H_5)_3PAuCl}^0 + RT[\ln P_{(C_2H_5)_3PAu} + \ln P_{Cl}] - \ln P_{(C_2H_5)_3PAuCl}] \quad V.15$$

Which reduces to

$$\Delta G = \Delta G^0 + RT \ln \frac{P_{(C_2H_5)_3Au} P_{Cl}}{P_{(C_2H_5)_3PAuCl}} \quad V.16$$

or at equilibrium ($\Delta G = 0$)

$$\Delta G^0 = -RT \ln K \quad V.17$$

To determine the variation of K with temperature, consider V.11 at constant pressure or

$$\left(\frac{\partial G}{\partial T} \right)_P = -S \quad V.18$$

From the relation

$$\left[\frac{\partial (G/T)}{\partial T} \right]_P = -\frac{1}{T^2} G + \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P \quad V.19$$

we can write from V.18

$$\left[\frac{\partial (G/T)}{\partial T} \right]_P = -\frac{1}{T^2} (G + TS) \quad V.20$$

which from V.8 becomes

$$\left[\frac{\partial (G/T)}{\partial T} \right]_P = -\frac{H}{T^2} \quad V.21$$

Applying this last result term by term to V.15 we have

$$\left[\frac{\partial(\Delta G/T)}{\partial T} \right]_P = - \frac{\Delta H}{T^2} \quad \text{V.22}$$

and also

$$\left[\frac{\partial(\Delta G^0/T)}{\partial T} \right]_P = - \frac{\Delta H^0}{T^2} \quad \text{V.23}$$

Substituting V.17 into this last result gives

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \quad \text{V.24}$$

Integration of V.24 gives

$$\ln K = A - \frac{\Delta H^0}{RT} \quad \text{V.25}$$

where A is an integration constant. Thus a plot of $\ln K$ versus $1/T$ should be linear with a slope of $\Delta H^0/R$ where ΔH^0 is the standard enthalpy change in going from adsorbed products to adsorbed reactants. For the equilibria expressed in Equation V.8, it is assumed that the adsorbed species exist as a two dimensional gas on the surface for which a standard state can be defined with an associated unitary pressure. For relative comparison of the surfaces it is not necessary to define these absolutely. Thus it is assumed that the surface pressure is proportional to the mass spectrometer species intensities from

$$[(C_2H_5)_3PAu] = [Cl] = aP_p = a(\text{chlorine isotope sum})$$

$$[(C_2H_5)_3PAuCl] = bP_r = b(\text{gold containing peak sum})$$

where a and b are proportionality constants and P_p and P_r are product and reactant pressures respectively in terms of the dimensions necessary for the establishment of the standard surface state. Equation V.25 becomes

$$\ln K - \ln \left(\frac{a^2 P_p^2}{b P_r} \right) = A - \frac{\Delta H^0}{RT} \quad \text{V.26}$$

Isolating the pressure terms on the left side the relation becomes

$$\ln \frac{P_p^2}{P_r} = B - \frac{\Delta H^0}{RT} \quad \text{V.27}$$

where $B = A + \ln(b/a^2)$.

Figures V.17 and V.18 are plots of $\ln(P_p^2/P_r)$ versus $1/T$ of runs on silicon and tungsten respectively (curves labeled A). Linear regression lines (curves labeled C) as well as a secondary Y axis plots (curves labeled B) of the surface heating profile ($1/T$ versus time) are also included. Linear regressions on both sets of data points were performed at points corresponding to 150°C and above. This temperature was chosen due to the apparent commencement of decomposition on tungsten near that point in the matrix studies. Thus the equations for the best fit line through these points from the linear regression are:

$$\ln P_p^2/P_r = 16.64 \pm 0.17 - 3614 \pm 90(1/T) \text{ for silicon}$$

Correlation Coefficient = 0.9373
191 observations

$$\ln P_p^2/P_r = 9.2 \pm 0.11 - 1293 \pm 44(1/T) \text{ for tungsten}$$

Correlation Coefficient = 0.9042
226 observations

The values for the coefficients imply that for the surface reaction on silicon the standard enthalpy change is 3 times that for the same reaction on tungsten. In other words, tungsten appears to lower the energy that must be supplied for the forward reaction by a factor of 3 relative to that of the reaction on silicon. This result is not surprising in view of the fact the observed selectivity calls for some substantial energy differences on the two surfaces. On the other hand, it has been tacitly assumed here that the surface retains the character of the respective substrate material. This is not the case since in each instance the surface is slowly changing to one of gold. It would be expected that the $\ln K$ versus $1/T$ plots would in time acquire curvatures, then become linear with a common slope. This was not observed since the deposition times were too short for the growth of substantially thick films. Most probably, this result reflects the nature of the relative surface topographies in terms of the presence of active sites available for adsorption. Since the silicon surfaces are engineered to reduce concentrations of defects in the bulk, this would seem to translate to the surface situation as well. The tungsten films, being polycrystalline and highly faceted, can offer a distribution of relatively high free energy defect sites to promote the apparent catalytic decomposition.

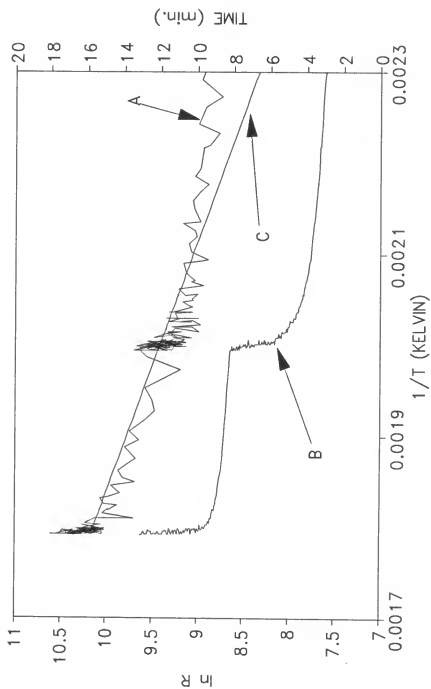


Figure V.10. Plot of $\ln R$ ($R = P_p^2/P_r$) versus $1/T$ for reductive elimination of chlorine from triethyl phosphine gold chloride on silicon.

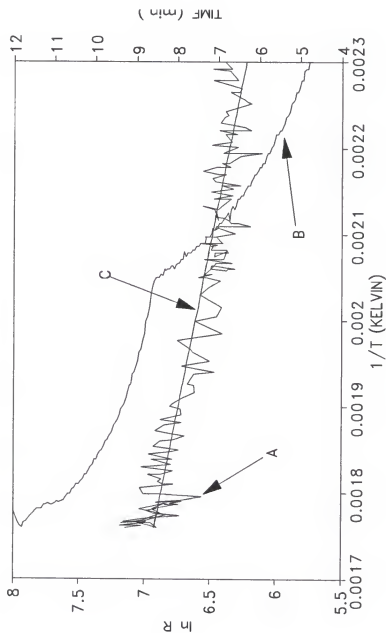


Figure V.11. Plot of $\ln R$ ($R = P_p^2/P_r$) versus $1/T$ for reductive elimination of chlorine from triethyl phosphine gold chloride on tungsten.

If the chlorine elimination reaction is the first step in decomposition of the gold carrier, then a simple triethyl phosphine detachment could follow. It has been stated above that the triethyl phosphine chloride signal shows surface sensitive responses implying a surface combination reaction. On the other hand, the triethyl phosphine signal also shows a surface sensitive response which suggests a simple elimination of the neutral ligand. Quantitative treatment of the surface behavior of triethyl phosphine in terms of a similar treatment for chlorine would be difficult from the data gathered in these experiments due to its abundant gas phase formation. Further experiments are necessary for verification of a detailed decomposition mechanism.

CHAPTER VI CONCLUSIONS AND RECOMMENDATIONS

The area selective CVD of gold on tungsten patterned on silicon has been demonstrated. The selective depositions seem to be controlled by an interplay between the relative kinetics of reactions on silicon and tungsten and physical barriers to the formation of stable condensates on silicon. All observations were explainable within the bounds of the theory presented.

The goal of this work was to study the feasibility and to develop the chemistry of the selective gold CVD scheme that had both utility as a replacement for aluminum interconnects in current usage and that would be amiable for the straightforward integration into existing process environments. These goals were substantially achieved. The utility of the gold on tungsten structure has already been discussed. The process itself should seem quite simple from its description since all that is necessary is the control of various process parameters during the exposure of a heated substrate to a flux of the carrier vapor. Vapor deposition apparatus now in commercial operation could conceivably be used for this process, possibly with little modification. It is anticipated that intensive investigation of the gold crystal growth and selectivity

relative to different surface modifications should allow for the solution of the grain coalescence problem while maintaining selective deposits. Solution of these problems should make this technology a very attractive interconnect formation alternative.

The work presently reported represents one on many possible combinations of metal carrier and substrate systems for selective CVD which could have technological importance. To be sure, this research did not touch on the varying of the gold carrier which should have profound effects on the nature of the films grown and the selectivity in general. Triethyl phosphine gold chloride represents one member of a homologous series of compounds which should be explored. Indeed, one branch of CVD is concerned with the development of new volatile carriers. The trends toward total in situ processing and miniaturization in micro and opto electronics will accelerate the need for new selective processes to be explored and developed.

APPENDIX
MASS SPECTROMETER CALIBRATION

Mass spectrometer calibration was performed after data was collected from experimental runs. This involved using a standard mass spectrum (Figure V.8) of the gold carrier compound and identifying that pattern in the raw captured data. The assumption was made that a linear relation existed between the raw data peak locations and the true mass to charge ratio. The raw data locations of triethyl phosphine gold, gold and triethyl phosphine were identified and a linear regression was performed as follows. The 12 bit resolution of the data acquisition adapter over 800 AMU resulted in 2048 data points in the experimental raw data (400 AMU scans). Several spectra captured during both experimental runs were analyzed and it appeared that peak maxima showed no variance with regards to their location in the spectra from scan to scan. Thus the peak maximum values were divided by 5.12 (2048/400). The following relations were found for triethyl phosphine, gold, and triethyl phosphine gold respectively:

Raw Data Peak Maximum	Raw Data Max. Divided by 5.12	True Location
588	114.84	118.09
986	193.58	196.97
1575	307.62	315.06

Linear regression yields

$$\text{Adjusted value} = 1.0227 \times (\text{Raw Data}/5.12) - 0.0281$$

The correlation coefficient from the linear regression is 1.0000. This relation was then used to identify all resulting peak locations from their maximum's raw value location.

REFERENCES

1. A. G. Sabnis, VLSI Electronics Microstructure Science, Vol. 15: VLSI Metallization, N. G. Einspruch, S. S. Cohen, and G. S. Gildenblat, eds. (Academic Press, Inc., Orlando, FL, 1987), p297.
2. See, for example, The Proceedings of the Sixth International IEEE VLSI Multilevel Interconnect Conference, (1989).
3. J. C. Blair, C. R. Fuller, P. B. Gbate, and C. T. Haywood, J. Appl. Phys., 43, 2, (1972).
4. S. O. Colgate, G. J. Palenik, V. E. House, and D. W. Schoenfeld, J. Vac. Sci. Technol. A, 8, 3 (1990).
5. R. H. Dennard, F. H. Gaensslen, N. H. Yu, V. L. Rideout, E. Bassous, and A. R. Leblane, IEEE J. Solid-State Circuits, 9(5), 256 (1974).
6. P. B. Gbate, Solid State Technology, 26(3), 113 (1983).
7. I Wagner, Y. H. Parks, and J. F. Smith, Transaction of the 47th and 48th Schools on Thin Film Technology: Advances in Magnetron Sputtering, (Materials Research Corp., Orangeburg, NY, 1990) Dps-VI-1.
8. H. B. Huntington and A. R. Grone, J. Phys. Chem. Solids, 25, 335 (1971).
9. F. M. d'Heurle and P. S. Ho, in Thin Films- Interdiffusion and Reactions, J. M. Poate, K. N. Tu, and J. W. Mayer, eds., (J. Wiley and Sons, New York, 1978), p243.
10. D. S. Gardiner, T. L. Michalka, T. W. Barbee, Jr., K. C. Saraswat, J. P. McVittie and J. D. Meindl, Proc. Int. IEEE Multilevel Interconnections Conf., 1st, New Orleans, La. pp 68-77 (1984).
11. S. Wolf, and R. N. Taber, Silicon processing for the VLSI Era: Volume 1--Process Technology, (Lattice Press, Sunset Beach, CA. 1986) Chap 10.

12. A. K. Sinha, J. Vac. Sci. Technol., 19(3), 778 (1981).
13. A. K. Sinha, Thin Solid Films, 90(3), 271 (1982).
14. B. Gorowitz, R. J. Sala, and E. W. Balch, VLSI Electronics Microstructure Science, Vol. 15: VLSI Metallization, N. G. Einspruch, S. S. Cohen, and G. S. Gidenblat, eds. (Academic Press, Inc., Orlando, FL, 1987), p426.
15. F. O. Sequeda, Journal of Metals, May, 43 (1985).
16. B. M. Welch, D. A. Nelson, Y. D. Shen and R. Venkataraman, VLSI Electronics Microstructure Science, Vol. 15: VLSI Metallization, N. G. Einspruch, S. S. Cohen, and G. S. Gidenblat, eds. (Academic Press, Inc., Orlando, FL, 1987), Chap. 9.
17. N. Awaya and Y. Arita, 1989 Symp. on VLSI Tech., Kyoto, Japan, p102.
18. F. A Houle, R. J. Wilson, and T. H. Baum, J. Vac. Sci. Technol. A 4, 6, (1986).
19. C. R. Mollan, T. H. Baum, and C. R. Jones, App. Phys. A, 40, 1 (1986).
20. K. Hoshino, H. Yagi, and H. Tsuchikawa, The Proceedings of the Sixth International IEEE Multilevel Interconnect Conference, p226 (1989).
21. P. L. Pai and C. H. Ting, The proceedings of the Sixth International IEEE VLSI Interconnect Conference, p258 (1989).
22. M. J. Hampden-Smith, T. T. Kotas, M. Paffett, J. D. Farr, and H. K. Shin, Chem. Mater. 2(6), 636, (1990).
23. E. Hokelek and G. Y. Robinson, Thin Solid Films, 53, 135, (1978).
24. C. Y. Ting and M. Wittmer, J. Appl. Phys., 54, 937, (1983).
25. N. E. Miller and I. Beinglass, Solid State Technol., 25, 12, (1982)
26. R. H. Wilson, R. W. Stroll, and M. A. Calcone, Tungsten and Other Refractory Metals for VLSI Applications, R. S. Blewer, ed., (Materials Research Society, Pittsburgh, Pennsylvania, 1986), pp35-42.

27. M. L. Green and R. H. Levy, J. Electrochem. Soc., 132, 1243 (1985).
28. J. E. J. Schmitz, R. C. Ellwanger, and J. M. van Dyk, Tungsten and Other Refractory Metals for VLSI Applications III, V. A. Wells, ed., (Materials Research Society, Pittsburg, Pennsylvania, 1986), pp. 35-42.
29. D. S. Cambell, Handbook of Thin Film Technology, L. I. Maissel and R. Glang, eds. (McGraw-Hill Book Company, Inc., New York, 1970), p5-1.
30. Y. P. Butylin, Ukr. Khim. Zh., 53(10), 1021 (1987).
31. C. Patton, Electronics Design, 46, 25, (1986)
32. F. Jansen, Plasma Deposited Thin Films, J. Mort and F. Jansen, eds. (CRC Press, Inc., Boca Raton, FL, 1986), p37.
33. R. A. Dugdale, Nature, 249, 440 (1974).
34. M. L. Green and R. A. Levy, J. Metals, June, 63 (1985).
35. T. Tagaki, J. Vac. Sci. Technol. A, 2, 282 (1984).
36. W. Knauer and R. L. Poeschel, J. Vac. Sci. Technol. B 6(1), 456 (1988).
37. D. W. Skelly, T. M. Lu, and D. W. Woodruff, VLSI Electronics Microstructure Science, Vol. 15: VLSI Metallization, N. G. Einspruch, S. S. Cohen, and G. S. Gidenblat, eds. (Academic Press, Inc., Orlando, FL, 1987), p119.
38. K. L. Wang, Solid State Technol. 28(10), 137 (1985).
39. E. Bunsen, J. prakt. Chem. 56, 53 (1852).
40. H. Saint-Claire Deville, Ann. 120, 176 (1861).
41. de Lodyguine, U. S. Patent 575,002 (1893).
42. A. E. van Arkel and J. H. de Boer, Z. anorg. u. allegen. Chem. Phys. 7(5), 742 (1925).
43. A. E. van Arkel, Metallwirtschaft 13, 405 (1934).
44. W. Blitz, W. Fischer, and R. Juza, Z. anorg. u. allgen Chem. 148, 345 (1925).
45. F. G. Mann, A. F. Wells, and D. Purdie, J. Chem. Soc. 2, 1828 (1937).

46. T. H. Baum, C. R. Jones, Appl. Phys. Lett. 47, 5381, (1985).
47. T. H. Baum, C. R. Jones, J. Vac. Sci. Technol., B 48, 1187, (1986).
48. T. H. Baum, E. E. Marinaro, C. R. Jones, Appl. Phys. Lett. 49, 1187, (1986).
49. R. J. Puddephatt and I Treurnicht, J. Organomet. Chem. 319, 129, (1987).
50. M. Berkenblit and A. Reisman, Met Trans. 2, 803 (1971).
51. D. J. Dumin, J. Cryst. Growth, 8, 33 (1971).
52. E. K. Broadbent and W. T. Stacy, Solid State Tech., 12, 51 (1985).
53. J. Y. Tsao and D. J. Ehrlich, J. Cryst. Growth 68, 176 (1984).
54. D. M. Brown, B. Gorowitz, R. Wilson, and R. Saia, IEEE Electron Device Lett. EDL-6, 408 (1985).
55. N. E. Miller and I Beinglas, Solid State Tech. 5, 293 (1985).
56. R. S. Blewer and V. A. Wells, Proc. Multilevel Metalization and Packaging Symp, p200, (1984).
57. E. K. Broadbent and C. L. Miller, J. Electrochem. Soc. 131(6), 1427 (1984).
58. R. L. Kubena, F. P. Stratton, and T. M. Mayer, J. Vac Sci and Technol., B 6(6), 1865 (1988).
59. S. Wolf, and R. N. Taber, Silicon processing for the VLSI Era: Volume 1--Process Technology, (Lattice Press, Sunset Beach, CA. 1986) Chap 6.
60. W. Kern and V. Ban, Thin Film Processes, J. L. Vossen and W. Kern, eds, p257 (Academic, New York, 1978).
61. M. Hammond, Solid State Technol. 12, 61 (1979).
62. W. Kern and G. L. Schnable, IEEE Trans. Electron Devices ED-26, 647 (1979).
63. P. Singer, Semiconductor International., 5, 250, (1984).
64. R. S. Rosler, Solid State Technol. 20(4), 63 (1977).

65. M. M. Faktor and I. Garret, Growth of Crystals From the Vapor, (Chapman and Hall, London, 1974) p193.
66. D. W. Shaw and C. H. L. Goodman, Crystal Growth-Theory and Technique, Vol.1, (Plenum, New York, 1974) p77.
67. U. Jansson and J. Carlson, J. Vac. Sci. Technol. A 6(3), 1733 (1988).
68. J. Y. Tsao and D. J. Ehrlich, Appl. Phys. Lett. 45(6), 617 (1984).
69. J. Y. Tsao and D. J. Ehrlich, J. Cryst. Growth 68, 176 (1984).
70. C. A. Neugebauer, Handbook of Thin Film Technology, L. I. Maissel and R. Glang, eds (McGraw-Hill Book Company, Inc., New York, 1970), p8-6.
71. W. Wienberg and R. Merrill, J. Chem Phys. 56, 2881 (1972).
72. R. Palmer, H. Saltburg, and J. Smith, J. Chem. Phys. 50, 4552 (1974).
73. S. Brass, D. Reed, and G. Erlich, J. Chem. Phys. 70, 5244 (1979).
74. F. O. Goodman, Phys. Chem Solids, 24, 1451 (1963).
75. J. E. Lennard-Jones, Proc. Royal Soc. London, A 163, 127 (1937).
76. M. Volmer and A. Weber, Z. Phys Chem., 119, 277 (1925).
77. R. Becker and W. Doering, Ann. Physik., 24, 719 (1935).
78. G. A. Somorjai, Chemistry in two Dimensions: Surfaces, (Cornell University Press, Ithica, NY 1981), p331.
79. H. F. Winters, J. Schaegeel, and D. Horne, J. Vac. Sci. Technol., 15(4), 115, (1978).
80. T. A. Shankoff and E. A. Chandross, J. Electrochem. Soc., 122(2), 294 (1975).
81. R. J. Puddephatt, The Chemistry of Gold, (Elsevier Scientific Publishing Co., Amsterdam 1978) , p58.
82. J. Davies and P. Simpson, Induction Heating Handbook, (McGraw Hill Book Company (UK) Limited, London 1979), p310.

83. V. P. Naberezhnykh, L. T. Tsymbal, and M. S. Purchinskii, Phys. Stat. Sol. (b) 44, 845 (1971).
84. G. Frommeyer, Phys. Stat. Sol. (a) 50, 517 (1978).
85. S. Idziak and U. Haeberlen, J. Mag. Res. 50, 281 (1982).
86. P. Clausing, Z. Physik 66, 471 (1931).
87. J. Vac. Sci. Technol. 8, 636 (1971).
88. C. J. Whitman, J. Chem. Phys. 20, 161 (1952).
89. J. W. Ward, J. Chem. Phys. 50, 1877 (1969).
90. B. R. Baker and B. J. Wood, J. Vac. Sci. Technol. 7, 206 (1970).
91. B. P. Mathur and S. O. Colgate, Phys. Rev. A 6, 1266 (1972).
92. S. Wolf and R. N. Taber, Silicon Processing for the VLSI Era: Volume 1--Process Technology, (Lattice Press, Sunset Beach, CA 1986) Chap 18.
93. V. D. Frechette, J. C. Pulver, and D. R. Rossington, J. Amer. Ceram. Soc. 64(8), 463 (1981).
94. F. H. Constable, Proc. Royal Soc. London A. 108, 355 (1925).
95. R. J. Madix, CRC Critical Reviews in Solid State And Materials Science, (CRC Press, Boca Raton 1978), p143.

BIOGRAPHICAL SKETCH

Victor Evan House was born in Hillsboro, Illinois on October 11, 1954. At the age of four he moved with his family to Terre Haute, Indiana where he attended both primary and secondary school. Following high school graduation he enrolled at Indiana State University. After a year or so, he decided to take a leave from education and pursued other interests, especially long distance running. It was during this period that he grew interested in biology as it related to exercise and eventually enrolled at Indiana State and took courses toward A major in the life sciences. Chemistry, of course, was one the courses and he soon realized that chemistry was the basis for the study of life itself. He changed his major to chemistry and upon experiencing classes in physical chemistry he decided on that area as one for specialization. During that same period he enrolled in the Cooperative Education program at Indiana State taking a part time job in the research and development laboratories of International Minerals and Chemicals Corporation. Here he worked as a research technician in several different area including studies of controlled release technology and one summer performing various studies in an animal laboratory. He eventually perused and accepted a

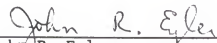
technicians position at IMC in physical chemistry and engineering research where he worked in electrochemical synthesis taking a project from the laboratory through to pilot operation. At the same time, he finished his undergraduate education graduating from Indiana State in May of 1985. In August of 1985 he enrolled in the graduate chemistry program at the University of Florida. There he studied under the direction of Prof. Samuel Colgate in the Physical Chemistry Division.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



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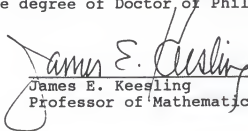
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